KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXII

N°. 1.

President: Prof. H. A. LORENTZ.

Secretary: Prof. P. ZEEMAN.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en Natuurkundige Afdeeling," Vol. XXVII).

CONTENTS.

H. B. A. BOCKWINKEL: "On MAC LAURIN's Theorem in the Functional Calculus" (Communicated by Prof. L. E. J. BROUWER), p. 2.

H. B. A. BOCKWINKEL: "Observations on the expansion of a function in a series of factorials". III. (Communicated by Prof. H. A. LORENTZ), p. 6.

H. B. A. BOCKWINKEL: "On the necessary and sufficient conditions for the expansion of a function in a Binomial Series". (Communicated by Prof. H. A. LORENTZ), p. 18.

H. P. BARENDRECHT: "Urease and the radiation-theory of enzyme action", III. (Communicated by Prof. J. BÖESEKEN), p. 29.

FRED. SCHUH: "A general definition of limit with application to limit-theorems". (Communicated by Prof. J. CARDINAAL), p. 46.

FRED. SCHUH: "A general definition of uniform convergence with application to the commutativity of limits". (Communicated by Prof. J. CARDINAAL), p. 48.

H. J. PRINS: "On the Condensation of Formaldehyde with some Unsaturated Compounds". (Communicated by Prof. J. BÖESEKEN), p. 51.

H. L. VAN DE SANDE BAKHUYZEN: "Photo-growth reaction and disposition to light in Avena sativa". (Communicated by Prof. F. A. F. C. WENT), p. 57.

P. H. VAN CITTERT: "The Structure of the Sun's Radiation". (Communicated by Prof. W. H. JULIUS), p. 73.

A. SMITS, G. L. C. LA BASTIDE, and J. A. VAN DEN ANDEL: "The Phenomenon after Anodic Polarisation". I. (Communicated by Prof. P. ZEEMAN), p. 82.

H. GROOT: "On the Effective Temperature of the Sun." Some remarks in connection with an article by DEFANT: "Diffusion und Absorption in der Sonnenatmosphäre". (Communicated by Prof W. H. JULIUS), p. 89.

Mathematics. — "*On* MAC LAURIN'S *Theorem in the Functional Calculus*". By Dr. H. B. A. BOCKWINKEL. (Communicated by Prof. L. E. J. BROUWER).

(Communicated in the meeting of March 29, 1919).

In the third communication of my paper "Some observations on complete transmutation" [1]) I proved a restricted validity of MAC LAURIN'S theorem in the Functional Calculus for a *normal* additive transmutation. A normal transmutation was defined by me as follows:

1. There is a functional field $F(T)$, the functions u of which *belong to* [2]) the very same circle (σ), and for these functions the transmutation T produces functions belonging to the very same circle (α), concentric with (σ).

2. All rational integral functions are included in the functional field.

3. The transmutation T is continuous in the pair of associated fields $F(T)$ and (α) [3]).

From 2 it can be derived that to any such transmutation T another transmutation P *formally* corresponds, which is given by

$$Pu = a_0 u + \frac{a_1 u'}{1} + \frac{a_2 u''}{2!} + \ldots + \frac{a_m u^{(m)}}{m!} + \ldots, \quad . \quad . \quad . \quad (1)$$

where the quantities $u^{(m)}$ are the derivatives of the subject of operation u and the quantities a_m functions of the numerical variable x, which by means of the formula

$$a_m = \xi_m - m_1 x \xi_{m-1} + \ldots + (-1)^m x^m \xi_0 \text{ [4])} \quad . \quad . \quad . \quad . \quad (2)$$

can be derived from the functions

$$\xi_k = T(x^k) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

[1]) These Proc. Vol. XIX N°. 6 and 8 and Vol. XX N°. 3—7, to be quoted as l.c.

[2]) A function *belongs* to a circle, if it is regular *within and on* it. The symbol (σ) means a circle with radius σ.

[3]) See for the definition of continuity l.c. Vol. XIX N°. 8, where also definitions are given of the expressions *functional field* (*F. F.*), *numerical field of operation* (*N. F. O.*) (here the circle (α)) and *numerical field of functions* (*N. F. F.*) (here the circle (σ)).

[4]) By m_k the binomialcoefficient of order k of the number m is meant.

which are the transmutated of the successive positive integral powers of x: the latter functions exist according to 2 and belong to the circle (α). The above-mentioned theorem of MAC LAURIN consists in stating the *equality* of the transmutations T and P, in a certain numerical field (α'), which is part of (α) or identical with (α), *if the further condition is added, that the latter transmutation is complete in* (α') [1]).

In this statement there is something unsatisfying, if we compare it with TAYLOR's theorem for the *Theory of Functions*. The latter asserts: "if a function, in a certain circle, has some specified properties (viz. a *definite* differential coefficient) it can be expanded in TAYLOR's series in that circle". It is therefore not necessary *to impose further conditions on that series*. Accordingly it would be desirable that also in the *Functional Calculus* the theorem might be stated in such a way that it were not necessary to impose any further condition on the series P corresponding to the given transmutation T, but that *such conditions were implied in the properties of* T. At the time it was our opinion that this was not the case. But now we are in a position to prove the following proposition:

The series corresponding to a normal additive transmutation represents a complete transmutation.

For simplicity we consider a circular domain (σ) round the origin as a centre and in this the infinite sequence of functions

$$1, x, x^2, \ldots x^m, \ldots \ldots \ldots \ldots \quad (4)$$

to which, by definition, the infinite sequence of transmuted

$$\xi_0, \xi_1, \xi_2 \ldots \xi_m, \ldots \ldots \ldots \ldots \quad (5)$$

corresponds, the latter functions being regular in a circular domain (α). If we denote by ε an arbitrarily small positive quantity, then the sequence of functions

$$1, \frac{x}{\sigma+\varepsilon}, \frac{x^2}{(\sigma+\varepsilon)^2}, \ldots \frac{x^m}{(\sigma+\varepsilon)^m}, \ldots \ldots \ldots \quad (6)$$

derived from (4) converges uniformly to zero in the domain (α). According to a simple property of continuity (l.c. II, n°. 11) the sequence of the transmuted of the latter functions, which, by the additive property of the transmutation, is represented by

---

[1]) A transmutation P, represented by a series of the form (1), is called by me *complete in a domain* (α), if there is a certain circle (ρ), concentric with (α), such that *all* functions belonging to (ρ) possess a transmuted, regular in (α). The minimum circle (β), which may be taken for (ρ), I called the domain *corresponding* to (α) (l.c. Vol. XIX, N°. 6).

$$\xi_0, \frac{\xi_1}{\sigma+\varepsilon}, \frac{\xi_2}{(\sigma+\varepsilon)^2}, \cdots \frac{\xi_m}{(\sigma+\varepsilon)^m}, \cdots \quad (6')$$

will converge uniformly to zero in the domain (α); because a normal transmutation is continuous in a pair of conjugate fields. For sufficiently large m-values we have therefore in all points of (α)

$$|\xi_m| < (\sigma+\varepsilon)^m \quad (7)$$

From the equation (2) it is now easily derived that an analogous inequality holds for the functions a_m occurring in the series (1), that is to say, that these functions, too, are less in value than the m^{th} power of a certain number independent of m. For if (7) is valid for $m > m_0$, we have by (2), $|x|$ being at most equal to α,

$$|a_m| < \sum_0^{m_0} m_k \alpha^{m-k} |\xi_k| + \sum_{m_0+1}^{m} {}_k m_k \alpha^{m-k} (\sigma+\varepsilon)^k$$

$$< \longleftrightarrow + \sum_0^{m} {}_k \longleftrightarrow$$

$$< \longleftrightarrow + (\sigma+\alpha+\varepsilon)^m$$

The first part of the second member of this inequality consists of a fixed number of terms, each of which is, for sufficiently large m-values, less than $(\alpha+\varepsilon)^m$, so that the same holds for their sum. The second part is greater than the latter quantity, hence we have for sufficiently large m-values at all points of the domain (α)

$$|a_m| < (\sigma+\alpha+\varepsilon)^m \quad (8)$$

and therefore also

$$\overline{\lim_{m=\infty}} |a_m|^{\frac{1}{m}} \leqq \sigma+\alpha \quad (8')$$

Thus the upper limit in the left-hand member of this inequality is *finite*, and this is (Vol. XIX, N°. 6) the very condition under which the transmuting series (1) is *complete* in the domain (α); moreover we infer that the corresponding domain (β) has a radius β, no greater than $\sigma+2\alpha$. For all functions u belonging to the circle $(\sigma+2\alpha)$ the series P therefore produces a transmuted function Pu in the domain (α), and this transmuted is equal to Tu, according to the functional theorem of Mac Laurin we gave in the form (Vol. XX, N°. 3):

If the series P, answering to a normal additive transmutation T, is complete in the circular domain (α) forming the N. F. O. of T, we have in this domain $Tu = Pu$ for such functions of the functional field $F(T)$ of T as belong to the circle (β) corresponding to (α).

But now that we have found that the series answering to a normal additive transmutation has *necessarily* the property of representing a *complete* transmutation, our theorem can be expressed in the following form, in which it is more really a "theorem of MAC LAURIN" for the functional calculus, the unsatisfying point mentioned above having disappeared:

A *normal additive transmutation can always, in its N. F. O.* (α), *be expanded in the functional series of* MAC LAURIN (1), *either for all functions of its F. F., or for a certain part of it, consisting of the functions belonging to a circle* $(\beta) > (\sigma)$, (σ) *being the N. F. F.; and the radius* β *is never greater than* $\sigma + 2a$.

Mathematics. — *"Observations on the expansion of a function in a series of factorials."* III. By Dr. H. B. A. BOCKWINKEL. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 3, 1919).

10. We shall now prove that the theorem of NIELSEN is *inexact.* For this we use the following lemma:

If the series $\sum_{0}^{\infty n} a_n$ *diverges in such a way that the upper limit of the sum*

$$s_n = \sum_{0}^{n m} a_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

for $n = \infty$ *is equivalent to* n^θ, *where* θ *is a certain positive number, then the series*

$$\sum_{0}^{\infty n} \frac{a_n}{n^\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

converges or diverges according as $\alpha > \theta$ *or* $\alpha < \theta$.

Summation by parts gives

$$\sum_{0}^{n m} \frac{a_m}{m^\alpha} = \frac{s_n}{n^\alpha} + \sum_{0}^{n-1 m} s_m \left(\frac{1}{m^\alpha} - \frac{1}{(m+1)^\alpha} \right). \quad . \quad . \quad . \quad . \quad (37)$$

For $\alpha > \theta$, the limit of the expression s_n/n^α is, by the hypothesis, zero for $n = \infty$. Further the upper limit, for $m = \infty$ of the general term of the series in the right-hand member is equivalent to $m^{-(1+\delta)}$, if δ is a certain positive number, so that the series converges if n is made infinite. So the series in the left-hand member, too, converges for $n = \infty$.

Again, writing

$$s_{\alpha,n} = \sum_{0}^{n m} \frac{a_m}{m^\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36')$$

we find on summation by parts

$$\sum_{0}^{n m} a_m \equiv \sum_{0}^{n m} m^\alpha \frac{a_m}{m^\alpha} = n^\alpha s_{\alpha,n} - \sum_{0}^{n-1 m} s_{\alpha,m} [(m+1)^\alpha - m^\alpha] \quad . \quad (38)$$

From this equality we may infer that, for $\alpha < \theta$, the upper limit

for $n = \infty$ of $s_{\alpha,n}$ is infinite, and is at least equivalent to $n^{\theta-\alpha}$. For, if this were not the case and if $s_{\alpha,n}$ were finite for $n = \infty$, or equivalent to a *lower* positive power of n, say $n^{\theta-\alpha-\delta}$, then the first term of the right-hand member would be of order $n^{\theta-\delta}$, whereas the terms of the series occurring in that member would be of order $m^{\theta-\delta-1}$, and their sum therefore at most of order $n^{\theta-\delta}$. This is in contradiction to the initial hypothesis that the left-hand member of the equality is of order n^{θ}.

The lemma has thus been proved. A corollary worthy of notice is that the series (36) for $\alpha < \theta$ diverges in such a way that the upper limit of the sum (36′) for $n = \infty$ is *exactly* equivalent to $n^{\theta-\alpha}$ (in the second part of our proof we found that it was *at least* equivalent to this power of n). For, if that limit were equivalent to a higher power of n, say $n^{\theta-\alpha+\delta}$, then the limit between convergence and divergence of the series

$$\sum_{0}^{\infty n} \frac{a_n}{n^{\beta}} = \sum_{0}^{\infty n} \left(\frac{a_n}{n^{\alpha}}\right) \frac{1}{n^{\beta-\alpha}}$$

would, by the proposition proved just now, be given by $\beta = \theta + \delta$, and not by $\beta = \theta$. The same consequence may, for the rest, be deduced by observing that from the equality (37) it follows that for $\alpha < \theta$ the left-hand member is *at most* equivalent to $n^{\theta-\alpha}$.

The same lemma as proved above holds for the series of factorials

$$\sum_{0}^{\infty n} \frac{n!\, a_n}{\Gamma(\alpha + n + 1)}, \quad \ldots\ldots\ldots \quad (39)$$

as may be proved in exactly the same way. Both lemmas are moreover a consequence of one another, because the series (36) and (39) converge and diverge for the same values of α, at least if α has not exactly the value θ, which is the limit between convergence and divergence of the series.

11. We now construct a sequence of coefficients

$$a_0, \quad a_1, \ldots a_n, \ldots\ldots\ldots \quad (40)$$

whose upper limit for $n = \infty$ is equivalent to n^{ρ}, whereas the upper limit of the sum (35) is equivalent to n^{θ}, θ now being a positive number less than 1. It is not difficult to effect this in different manners; but we shall moreover try to secure that the *second* sum quantity

$$s_n^{(2)} = \sum_{0}^{n m} s_m \quad \ldots\ldots\ldots \quad (41)$$

becomes of an order which is by *less than one unity* higher than the *first* sumquantity (35), i. e. of an order less than $n^{\vartheta+1}$. We proceed in the following way. For a certain value $n=p$ we take

$$s_p = \underline{p^\vartheta},$$

where by the notation $\underline{p^\vartheta}$ the same thing is meant as $E(p^\vartheta)$. Now we make the following sums decrease as soon as possible by taking a certain number of coefficients a_n, for $n>p$, all equal to -1. After $\underline{p^\vartheta}$ terms the sum s_n has in this way become equal to zero. And after $\underline{p^\vartheta}$ terms more s_n has attained the value $-\underline{p^\vartheta}$; the value of n is then equal to $p+2\underline{p^\vartheta}$. It may happen that for this value of n the quantity $\underline{n^\vartheta}$ is still equal to $\underline{p^\vartheta}$ [1]). In this case we may say that $|s_n|$ has again reached the required upper limit and we assume a certain number of next coefficients a_n all equal to $+1$. If, on the contrary, $\underline{n^\vartheta}$ for $n=p+2\underline{p^\vartheta}$ is greater than $\underline{p^\vartheta}$, we go on taking a_n equal to -1 as long as s_n has diminished to such an effect that $|s_n|$ is again equal to $\underline{n^\vartheta}$. Such an n-value *must* be reached, if $\vartheta<1$, for $|s_n|$ would become of order n, if we never stopped taking $a_n=-1$. Just as in the former case we assume, after this n-value, the next coefficients a_n equal to $+1$, until s_n has attained the value $\underline{n^\vartheta}$ again. And so on. The upper limit for $n=\infty$ of the sums s_n is then equivalent to n^ϑ and that of the coefficients a_n is equivalent to n^0. We call the values of n for which s_n is equal to $\underline{n^\vartheta}$ *critical* values and we denote them by n_k for $k=1, 2, \ldots$. If we assume arbitrarily a certain value $n=p$ as a critical value, then it follows from the preceding construction that the following critical values are uniquely determined. We might continue the same construction towards the side of the *smaller* n-values, but this is of no importance, since the *asymptotic* behaviour of the quantities in question is solely effective. The graphical representation of the coefficient a_n, considered as a function of n, consists of a number of horizontal line-segments, which are alternately above and beneath the n-axis, and are at a distance 1, the change taking place in the critical points. The graphical representation of the sums s_n consists of joined line-segments including alternately angles of $+\frac{\pi}{4}$ and $-\frac{\pi}{4}$ with the n-axis; and the alternation again takes place in the

[1]) We may write $(p+2\underline{p^\vartheta})^\vartheta = p^\vartheta + 2\vartheta p^{2\vartheta-1}(1-\varepsilon)$, where $\lim_{p=\infty} \varepsilon = 0$. From this it follows that for $\vartheta<\frac{1}{2}$ and large p-values, $E(p+2p^\vartheta)^\vartheta$ is *in general* equal to $E(p^\vartheta)$.

critical points, where the tops of the lines lie *within* the parabolic curve $y = \pm n^{\theta}$, at a distance less than unity from this curve.

We shall now shew that the upper limit for $n = \infty$ of the *second* sumquantities (41) is equivalent to $n^{2\theta}$. The sums

$$\sum_{n_k - \underline{n_k^{\theta}}}^{n_k} s_m \quad \text{and} \quad \sum_{n_k + 1}^{n_k + \underline{n_k^{\theta}}} s_m$$

are arithmetical progressions consisting of terms of equal signs only; their total value is easily verified to be exactly equal to $\pm (\underline{n_k^{\theta}})^2$. Thus we have, but for a certain constant, whose value is of no importance for the asymptotic behaviour of these sums:

$$\sum_{0}^{n_k + \underline{n_k^{\theta}}} s_m = (\underline{n_1^{\theta}})^2 - (\underline{n_2^{\theta}})^2 + \ldots \pm (\underline{n_k^{\theta}})^2$$

Since the terms of the sum in the right-hand member increase in absolute value or remain constant over a certain number of n-values, the sum itself is, in absolute value, less than the last and the first term together. So we have

$$\left| s^{(2)}_{n_k + \underline{n_k^{\theta}}} \right| < (\underline{n_k^{\theta}})^2 + (\underline{n_1^{\theta}})^2 < (\underline{n_k^{\theta}})^2 (1 + \varepsilon)$$

where ε is a positive quantity which tends to zero for $k = \infty$. Further, for an n-value lyiug in the interval between $n_k - \underline{n_k^{\theta}} = n_{k-1} + \underline{n_{k-1}^{\theta}}$ and $n_k + \underline{n_k^{\theta}}$ the value of $s^{(2)}_n$ lies *between* the two values of $s^{(2)}_n$ for these two limits, because s_n remains of the same sign between them, and therefore $s^{(2)}_n$ varies *monotonely*. So we have for *all* n- values of the interval considered

$$\left| s^{(2)}_n \right| < (\underline{n_k^{\theta}})^2 (1 + \varepsilon) \leqq n_k^{2\theta} (1 + \varepsilon).$$

For the part of the n-values greater than n_k we therefore have *a fortiori*

$$\left| s^{(2)}_n \right| < n^{2\theta} (1 + \varepsilon). \quad \ldots \ldots \ldots \quad (42)$$

For the remaining part we have

$$n \geqq n_k - \underline{n_k^{\theta}}.$$

Now

$$n_k^{2\theta} = (n_k - \underline{n_k^{\theta}} + \underline{n_k^{\theta}})^{2\theta} = (n_k - \underline{n_k^{\theta}})^{2\theta} (1 + \varepsilon)$$

where, again, ε is arbitrarily small for sufficiently great k. Thus for the latter n-values, too, we have

$$\left|s_n^{(2)}\right| < n_k^{2\theta}(1+\varepsilon) < (n_k - \underline{n_k^{\theta}})^{2\theta}(1+\varepsilon) < n^{2\theta}(1+\varepsilon). \quad . \quad (42')$$

The inequalities (42) show that the upper limit of $s_n^{(2)}$ for $n = \infty$ is, indeed, *at most* equivalent to $n^{2\theta}$. On the other hand it is easily seen that $n^{2\theta}$ is *exactly* the power of n to which the upper limit of $s_n^{(2)}$ for $n = \infty$ is equivalent, but this is of no importance for our purpose.

We now construct a function $\varphi(t)$ by means of the so-determined series of coefficients (40)

$$\varphi(t) = \sum_0^{\infty n} a_n t^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For this we may also write

$$\varphi(t) = (1-t) \sum_0^{\infty n} s_n t^n = (1-t)^2 \sum_0^{\infty n} s_n^{(2)} t^n \quad . \quad . \quad (43)$$

The last member of this equality shews of what order $\varphi(t)$ is at most for $t = 1 - \delta$. Since we have seen just now, that the upper limit of $s_n^{(2)}$ for $n = \infty$ is at most equivalent to $n^{2\theta}$, the function

$$\sum_0^{\infty n} s_n^{(2)} t^n$$

is, for $t = 1$, at most of order $1 : (1-t)^{1+2\theta}$. Hence $\varphi(t)$ is for $t = 1$ equal to zero, if $\theta < \frac{1}{2}$, and for $\frac{1}{2} < \theta < 1$ at most of order $1 : (1-t)^{2\theta-1}$. Thus we have

$$\lambda = 0 \quad \text{for} \quad \theta \leqq \tfrac{1}{2}$$
$$\lambda = 2\theta - 1 \quad \text{for} \quad \theta > \tfrac{1}{2}.$$

Since $2\theta - 1 = \theta - (1-\theta)$ and $\theta < 1$, we have in *both* cases

$$\lambda < \theta.$$

From the lemma proved in the preceding paragraph it now follows, since the upper limit of s_n for $n = \infty$ is equivalent to n^{θ}, that the series of factorials

$$\Gamma(x) \sum_0^{\infty n} \frac{n!\, a_n}{\Gamma(x+n+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

diverges for $R(x) < \theta$. *Hence it is not true here that this series converges for* $R(x) > \lambda'(=0)$ *and* $R(x) > \lambda$, *and a fortiori not that a certain integral of the form* (1), *for all such values of* x, *might be expanded in such a series. Therefore* NIELSEN'S *theorem is inexact.*

12. It is convenient to observe on this occasion that by means of the proposition of N°. 10 we may infer from the first part of formula (43) that never convergence of the series of factorials (6) takes place for $R(x) < \lambda$, a truth already shewn in another way in N°. 9 of the preceding communication.

For, if the upper limit of s_n for $n = \infty$ is equivalent to n^θ, then the function represented by the series

$$\sum_0^\infty {}_n\, s_n\, t^n$$

is, for $t = 1$, at most of order $1 : (1-t)^{1+\theta}$ and hence $\varphi(t)$ is at most of order $1 : (1-t)^\theta$, so that the number λ is not greater than θ, whereas the limit between convergence and divergence of the series of factorials according to the lemma mentioned, is afforded by $R(x) = \theta$.

13. At the end of the first communication we said that, if a certain argument mentioned there and used by NIELSEN were not erroneous, then another very general case of the possibility of expanding the integral

$$\Omega(x) = \int_0^1 \varphi(t)\,(1-t)^{x-1}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in a series of factorials would be proved by it, viz. the case when the series of factorials *corresponding to that integral* converges. We shall now prove that this case, though not established by NIELSEN, is, indeed, exact. In order to do this we shall make use of the following lemmas:

1. *If the series of factorials converges for a certain value $x = c$, then it converges for any value of x whose real part $R(x)$ is greater than that of c.*

Let

$$\sum_n^l {}_m \frac{m!\,a_m}{\Gamma(c+m+1)} = s_{n,l}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

then we find on summation by parts

$$\sum_n^l {}_m \frac{m!\,a_m}{\Gamma(x+m+1)} \equiv \sum_n^l {}_m \frac{m!\,a_m}{\Gamma(c+m+1)} \cdot \frac{\Gamma(c+m+1)}{\Gamma(x+m+1)} =$$

$$= \frac{s_{n,l}\,\Gamma(c+l+1)}{\Gamma(x+l+1)} + (x-c) \sum_n^{l-1} {}_m \frac{s_{n,m}\,\Gamma(c+m+1)}{\Gamma(x+m+2)}.$$

On account of the supposed finiteness of $s_{n,\infty}$, the limit of the first term of the last member is for $R(x) > R(c)$ equal to zero, if l increases indefinitely and the series in that member converges absolutely. Hence the series in the first member converges also and we have

$$\sum_{n}^{\infty m} \frac{m!\, a_m}{\Gamma(x+m+1)} = (x-c) \sum_{n}^{\infty m} \frac{s_{n,m}\, \Gamma(c+m+1)}{\Gamma(x+m+2)} \quad . \quad . \quad (45)$$

by which the lemma is proved. It follows from it that *the limit between the domain of convergence and the domain of divergence of a series of factorials is formed by a straight line parallel to the imaginary axis.*

Moreover we may infer from the equality (45) the following lemma:

II. *In any finite part S of the half-plane* $R(x) > R(c) + \delta$, δ *being a fixed, but arbitrarily small real positive quantity, the series of factorials converges uniformly.*

For n may be chosen so large, corresponding to any arbitrarily given ε, that for all $m \geqq n$

$$\left| \frac{s_{n,m}\, \Gamma(c+m+1)}{\Gamma(x+m+2)} \right| < \frac{\varepsilon}{m^{R(x-c)+1}}$$

and thus

$$\left| (x-c) \sum_{n}^{\infty m} \frac{s_{n,m}\, \Gamma(c+m+1)}{\Gamma(x+m+2)} \right| < \frac{\varepsilon\, |x-c|}{R(x-c)\, n^{R(x-c)}} \quad . \quad . \quad (46)$$

Since $R(x-c) \geqq \delta$, the right-hand member of this inequality is, for a sufficiently large n-value, *which is independent of the value of* x *in the domain* S, less than ε. This was to be proved.

From the inequality (46) we may infer the corollary II*a*: *If the series of factorials* (6) *converges for a certain value* $x = c$, *then it converges uniformly on the half-line beginning at* $x = c$ *and having the direction of the positive part of the real axis.*

For on this line $R(x-c) = x-c$; hence the right-hand member of (46) passes into $\varepsilon : n^{R(x-c)}$ and this is less than ε independently of the place of x on that line. The corollary is an analogon of a well-known proposition of ABEL on the *uniform* convergence of a *power-series* along the radius of a certain point of its circle of convergence, if that power-series converges at that point.

From lemma II, in connection with the fact that the terms of the series of factorials (6) are *continuous* functions of x, it may be inferred that such a series represents a *continuous* function of x in the domain

S, even in case S lies wholly or partly in the domain of only *conditional* convergence; of course it must be supposed that all points of S lie at a distance greater than some *fixed* arbitrarily small quantity δ from the straight line parallel to the axis of imaginary quantities which forms the limit between the domains of convergence and divergence of the series. Finally we shall prove that this series represents an *analytic* function in S, and for this it will be sufficient to show that the series of differential coefficients, with regard to x, of the terms of the first series converges in the same domain as this first series.

The series of derivatives may be represented by

$$-\Gamma(x)\sum_{0}^{\infty}{}_{n}\frac{n!\,a_n}{\Gamma(x+n+1)}[\psi(x+n+1)-\psi(x)]. \quad . \quad (47)$$

where, in the notation of NIELSEN [1]), $\psi(x)$ denotes the logarithmic derivative of the Gammafunction:

$$\psi(x)=\frac{d\log\Gamma(x)}{dx}=\frac{\Gamma'(x)}{\Gamma(x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

Summation by parts gives, if the notation (44) is used again

$$\sum_{n}^{l}{}_{m}\frac{m!\,a_m\psi(x+m+1)}{\Gamma(x+m+1)}\equiv\sum_{n}^{l}{}_{m}\frac{m!\,a_m}{\Gamma(c+m+1)}\cdot\frac{\Gamma(c+m+1)\,\psi(x+m+1)}{\Gamma(x+m+1)}=$$

$$=\frac{s_{n,l}\,\Gamma(c+l+1)\,\psi(x+l+1)}{\Gamma(x+l+1)}+\sum_{n}^{l-1}{}_{m}\frac{s_{n,m}\Gamma(c+m+1}{\Gamma(x+m+2)}[(x-c)\psi(x+m+2)-1],$$

where the equation of finite differences

$$\psi(x+1)-\psi(x)=\frac{1}{x}$$

satisfied by $\psi(x)$ is taken into account. Since, for $x=\infty$ the principal part of $\psi(x)$ is equal to $\log x$, the first term of the second member has, for $R(x-c)\geq\delta$, zero as a limit for $l=\infty$, and the series in that member converges absolutely. Hence the series in the first member converges also and we have

$$\sum_{n}^{\infty}{}_{m}\frac{m!\,a_m\psi(x+m+1)}{\Gamma(x+m+1)}=\sum_{n}^{\infty}{}_{m}\frac{s_{n,m}\Gamma(c+m+1)}{\Gamma(x+m+2)}[(x-c)\psi(x+m+2)-1].$$

From this equality it may be easily deduced that, corresponding to any ε, there is a number N such that for $n>N$ and for all x in the domain S

[1]) Handbuch der Gammafunktion, p. 15, Leipzig, Teubner.

$$\left| \sum_{n}^{\infty}{}_{m} \frac{m!\, a_m \psi(x+m+1)}{\Gamma(x+m+1)} \right| < \frac{\varepsilon \log n}{\delta n^{\delta}}$$

that is $< \varepsilon$, since $(\log n) : n^{\delta}$ is zero for $n = \infty$. By this the convergence of the first part of the series of derivatives (47) has been proved, together with the *uniform* convergence in S. The second part need not be examined more closely, since this part forms a series which, save as to the factor $\psi(x)$ not depending on n, is equal to the series of factorials itself.

On account of its uniform convergence in the domain S and the continuity of its individual terms the series of derivatives in question represents in S the derivative of the function determined by the original series of factorials. The differential coefficient of this function is therefore determined at any point of S, and is independent of the direction in which it is taken: thus *the series of factorials represents an analytic function in the domain S.*

14. We now proceed to settle the question indicated at the beginning of the preceding section, and we first consider the case $\lambda' = 0$, in which the upper limit of a_n for $n = \infty$ is equivalent to n^0. We further assume the limit of convergence and divergence of the series (6) to be given by $R(x) = \theta$, θ being a positive number less than unity. Since, as we showed, the number λ is in any case not greater than θ, we have

$$\lim_{t=1} (1-t)^x \varphi(t) = 0 \quad \text{for} \quad R(x) > \theta.$$

From this it follows that the integral (1) converges absolutely for $R(x) > \theta$. At the same time this convergence is *uniform* in any domain S wholly included in the finite part of the half-plane $R(x) > \theta + \delta$, where δ is a certain fixed, but for the rest arbitrarily small positive number. The same holds for the integral

$$\int_0^1 \varphi(t)\,(1-t)^{x-1} \log(1-t)\, dt,$$

which may be deduced from the integral (1) by differentiating the latter under the integration-sign with regard to x. Hence this integral represents in S the derivative with regard to x of the integral (1), so that the latter is an *analytic* function of x in the domain S. [1])

[1]) The statements mentioned here briefly have been established by PINCHERLE in his paper "*Sur les fonctions déterminantes*", Ann. de l'Éc. Norm. (3) XXII, 1905, p. 13—17. Their analogy with those we proved in the preceding section is manifest.

Now, the two analytic functions represented by the integral (1) and by the factorial series (6) are known to be equal in the domain of *absolute* convergence of that series, formed by the half-plane $R(x) > 1$. According to a well-known theorem of the theory of functions they *cannot therefore differ in the domain of only conditional convergence*

$$\theta < R(x) \leqq 1.$$

Thus the indicated proposition has been proved in the definite case $\lambda' = 0$. Further, if $\lambda' > 0$ and the limit of the domains of convergence and divergence of the series (6) be given by

$$R(x) = \lambda' + \theta,$$

then, again, $\lambda \leqq \lambda' + \theta$, as we proved as well in the preceding communication; and similar statements as before hold with regard to the integral (1), which therefore is again equal to the series of factorials in its domain of *conditional* convergence

$$\lambda' + \theta < R(x) \leqq \lambda' + 1,$$

as well as in its domain of *absolute* convergence. If, at last, λ' and $\lambda' + \theta$, the limit between convergence and divergence of the series of factorials, are both negative, then the integral (1) in general exists only for $R(x) > 0$, but in this case the series affords the *analytic continuation* of the integral in the part of the plane given by

$$\lambda' + \theta < R(x) \leqq 0.$$

We may also say that a certain *remainder* of the series (6) is represented by an integral of the form

$$\int_0^1 \varphi^{(p)}(t)\,(1-t)^{x+p-1}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in the whole domain of convergence of the series.

We thus have proved the theorem: *A series of factorials, whose domain of convergence is the half-plane on the right of the line* $R(x) = \xi$, *is represented in a possibly existing domain of only conditional convergence by the same integral of the form* (1) *as in the domain of absolute convergence, if* $\xi \geqq 0$. *If, however,* $\xi < 0$, *the same relation exists between a certain remainder of the series and an integral of the form* (8).

15. Finally we shall give a small correction and complement to the last two parts of N°. 6 in the second communication. The clause: "if it (the function) is continuous and "à écart fini" on that circumference, or *if a certain derivative of negative order* — ω *has this property*", contains an in-correctness because the possibility might be

inferred from it, that sometimes *not* a certain derivative had that property. This is not the case; if the characteristic λ', defined by (14), of the coefficients a_n in the power-series for the function $\varphi(t)$ is *finite*, this function always has a derivative of a certain order $-\omega$ possessing the property in question and we have

$$\omega = \lambda' + 1.$$

Further it is shown by HADAMARD [1]), that a function $\varphi(t)$, which is of order ω with regard to the *whole* circumference, and of *lower* order ω_0 on a certain part of it containing the point $t=1$, can always be divided into two functions $\varphi_1(t)$ and $\varphi_2(t)$, the first of which is *regular* at $t=1$ and of order ω on the whole circumference, and the other of order ω_0 on the whole circumference. According to the theorem proved in the same N°. 6 the integral

$$\int_0^1 \varphi_1(t)\, t^{x-1}\, dt,$$

c.q. an integral with $\varphi_1^{(p)}(t)$ as subject of integration, can, for $R(x) > \omega - 1 = \lambda'$, be expanded in a series of factorials. Further the integral

$$\int_0^1 \varphi_2(t)\, t^{x-1}\, dt$$

c.q. an integral containing $\varphi_2^{(q)}(t)$, can be expanded in such a series for $R(x) > \omega_0$. Hence the integral (1), being the sum of the two preceding integrals, c.q. an integral containing $\varphi^{(r)}(t)$, can be expanded in a series of factorials for

$$R(x) > \omega_0 \quad \text{or} \quad R(x) > \lambda',$$

according as ω_0 or λ' has a greater value. In the first case the series converges *conditionally* for

$$\omega_0 < R(x) < \lambda' + 1,$$

and in the second for

$$\lambda' < R(x) < \lambda' + 1.$$

In both cases we may state the following proposition:

If ω is the order of $\varphi(t)$ along the whole circle of convergence, and therefore $\lambda' = \omega - 1$ the characteristic of its coefficients, and if ω_0 is the order of $\varphi(t)$ at the point $t=1$ of that circle, then the integral (1) (*c. q. the integral* (8)) *can be expanded in a series of factorials for such values of x as satisfy at the same time the inequalities*

$$R(x) > \lambda' \quad \text{and} \quad R(x) > \omega_0.$$

[1]) „Essai sur l'étude des fonctions", Journ. de Math., 1892, p. 172.

We cannot say, however, that this proposition *is a substitute* for that of NIELSEN, because a series of factorials sometimes converges for $R(x) < \omega_0$. Take, for instance, the function of WEIERSTRASS

$$\varphi(t) = 1 + t^2 + t^4 + t^8 + \ldots + t^{2^k} + \ldots$$

This function has its circle of convergence as a *natural limit*, because all parts of the circumference are equivalent, as appears from the substitution

$$t = t' e^{\frac{2\pi ih}{2^k}},$$

where k and h are arbitrary integral numbers. The order ω_0 *in the point* $t = 1$ cannot, therefore, differ from the order ω along the *whole* circumference, and this order is equal to 1, the characteristic λ' of the coefficients of the power-series being zero. The quantity λ is, however, also zero and the series of factorials converges for $R(x) > 0$ and is, for all these values of x, equal to the integral (1) [1].

[1]) The convergence of the series of factorials is, in this case, *absolute*, in the strip of plane $0 < R(x) < 1$, owing to the large distance between the coefficients of $\varphi(t)$ which differ from zero. If, therefore, we spoke continually in the preceding investigations of *conditional* convergence for $R(x) < \lambda' + 1$, we meant this *in general*.

Mathematics. — *"On the necessary and sufficient conditions for the expansion of a function in a Binomial Series"*. By Dr. H. B. A. BOCKWINKEL. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 3, 1919)

PINCHERLE has given a necessary and sufficient condition for the expansion of a function in a *binomial series* (*Binomialkoeffizientenreihe*) [1]). It runs thus:

The necessary and sufficient condition that an analytic function $\omega(x)$ *may be expanded in a series of the form*

$$\omega(x) = \sum_{0}^{\infty}{}_{n} \; c_n \binom{x-1}{n} \quad . \; . \; . \; . \; . \; . \; . \; (1)$$

is that $\omega(x)$ *be* $coefficient\text{-}function$ (*fonction coefficiente*) *of another analytic funtion* $\varphi(t)$, *which is regular and zero at infinity and whose singularities lie all within the circle* $(1,1)$, *with centre* $t=1$ *and radius* $r=1$, *or on the circumference of it, provided that, in the latter case, the order of* $\varphi(t)$ *on the circumference, taken in the sense defined by* HADAMARD, *be finite or negative infinite* [2]).

By a coefficientfunction $\omega(x)$ of an analytic function $\varphi(t)$ of the kind mentioned PINCHERLE means a function which can be deduced from $\varphi(t)$ in a more or less simple manner, according to the order of $\varphi(t)$. The relation between the two functions is, however, always such that conversely $\varphi(t)$, called by PINCHERLE the *generating* function (fonction génératrice) of $\omega(x)$, follows from $\omega(x)$ by the equation

$$\varphi(t) = \sum_{0}^{\infty}{}_{n} \frac{\omega(n+1)}{t^{n+1}}, \; . \; . \; . \; . \; . \; . \; . \; (2)$$

This means: the *coefficients* of the series of negative integral powers of t, in which $\varphi(t)$ may be expanded in a neighbourhood of $t=\infty$, are equal to the values of $\omega(x)$ for positive integral values of x; the name *coefficientfunction* for $\omega(x)$ is due to this circumstance.

The question now arises, how it must be discriminated if a *given* function may oe expanded in a binomial series. *This question is not*

---

[1]) S. PINCHERLE, "Sur les fonctions déterminantes", Annal. de l'Ecole Normale, 1905.

[2]) A circle with centre α and radius r will be denoted by (α, r).

answered by the theorem of PINCHERLE, at least not in a simple manner, as will appear from what follows. In order to investigate the question we should commence to deduce the series (2) from the given function $\omega(x)$. Next we should examine whether the function $\varphi(t)$ represented by it has the required properties: to be regular without the circle (1,1), and on the circumference of it of finite order. For this we should try to transform the above series into another according to negative integral powers of $t-1$

$$\varphi(t) = \sum_{0}^{\infty} \frac{c_n}{(t-1)^{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The relation between the coefficients of the two series is given by the equations

$$c_n = \omega(n+1) - \binom{n}{1}\omega(n) + \ldots + (-1)^n \omega(1) = \Delta^n[\omega(1)]^{1}) \quad . \quad (4)$$

and

$$\omega(n+1) = c_0 + \binom{n}{1} c_1 + \ldots + c_n \quad . \quad . \quad . \quad . \quad (4')$$

By means of (4) we must see if the series (3) converges without the circle (1,1), and further if the *characteristic* λ' of the coefficients c_n, defined by

$$\lambda' = \overline{\lim_{n=\infty}} \frac{\log |c_n|}{\log n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

is not positive infinite; the latter being the condition that $\varphi(t)$ shall be of non-positive infinite order on the circle (1,1).

But the relation (4) is rather intricate and so it may be very difficult, if not impossible, to perform the just mentioned research. Suppose this, however, possible, and let λ' differ from $+\infty$. Then we have to examine whether the given function $\omega(x)$ is really the coefficientfunction of $\varphi(t)$. For there are a great many functions $\Omega(x)$ giving rise to the *same* generating function $\varphi(t)$, viz. all those contained in the equation

$$\Omega(x) = \omega(x) + F(x)$$

where $F(x)$ is a function that *vanishes* for positive integral values of x. It is therefore necessary to consult the definition of the coefficient-function given by PINCHERLE and to apply it to the obtained $\varphi(t)$ in order to see if the original function $\omega(x)$ is the result. But this is again not very easy. If the characteristic λ' defined by (5) is less than -1, then $\varphi(t)$ is finite and continuous along the circum-

[1]) This symbol denotes the n-th difference of $\omega(x)$ at $x=1$, the increase Δx of the argument x being equal to unity.

ference of the circle (1,1). The coefficient-function is then defined by the integral

$$\frac{1}{2\pi i}\int_{(1,1)} \varphi(t)\, t^{x-1}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

taken round the just mentioned circle, and this integral is easily seen to be equal to the binomial series (1) in the half-plane of x on the right of the imaginary axis, provided definite agreements as to the value of t^{x-1} be made. It may, however, be difficult to investigate whether the integral (6) is equal to the given function $\omega(x)$. And in any case the investigation is intricate if $\lambda' > -1$, especially when the difference between λ' and -1 is rather great. For the coefficient-function of $\varphi(t)$ is then brought into relation with that of another generating function, with $\lambda' < -1$, by means of a polynomial consisting of a very large number of terms.

The question therefore naturally suggests itself, if it is possible, to find simpler tests which are *sufficient* for a function to be expanded in a binomial series. This is, indeed, the case, and we may, moreover, say that the obtained properties are about *necessary* [1]). For we can prove the following theorem:

If a function $\omega(x)$ *is regular in the finite part of the half-plane* $R(x) \geqq \gamma$ [2]) $(\gamma = real)$, *and if, in that domain, it satisfies the inequality*

$$|\omega(x)| < M\,|(x+b)^l\, a^{x-\gamma}|\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where M *is a positive and* l *and* b *are real numbers, the latter such that* $b+\gamma > 0$, *further* a *a complex number on the circumference of the circle* (1,1), *variable with the argument* ψ *of* $x-\gamma$, *the argument* α *of* a *being equal to* $-\psi$ *so that*

$$a = 2\cos\psi\, e^{-i\psi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

then, in the domain $(\beta = real > \gamma)$.

$$R(x) > l + \beta - \tfrac{1}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

---

[1]) For the sake of comparison we observe that for the expansion of a function in a *series of factorials*

$$\sum_0^\infty{}_n \frac{n!\, a_n}{x(x+1)\,.\,.\,.\,(x+n)}$$

there is a necessary and sufficient condition, stated by Nielsen and simplified by Pincherle, which has some similarity with the above condition for binomial series. But it is not possible to find *simple* tests for the expansion of a function in a series of factorials. The only simple *sufficient* condition which may be given in this case, is that a function can be expanded in a series of factorials, if it is *regular and of zero value* at infinity. But this condition is far from necessary.

[2]) $R(x)$ means the real part of x.

the function $\omega(x)$ *can be expanded as a binomial series*

$$\omega(x) = \sum_{0}^{\infty}{}_n \, c_n \binom{x-\beta}{n}^{1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

if $l + \beta - \frac{1}{2} \geqq \gamma$, *and otherwise the expansion is possible in the domain* $R(x) \geqq \gamma$.

The special value $-\psi$ of the argument a of a is such that the expression $a^{x-\gamma}$, $x-\gamma$ being given, has the greatest modulus compared to those for other values of a on the circumference of the circle (1,1). *If the inequality* (7) *holds for fixed a-value on the circle* (1,1), *then expansion of* $\omega(x)$ *in the series* (10) *is possible in the domain*

$$R(x) > l + \beta - 1 \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9')$$

if $l + \beta - 1 \geqq \gamma$, *and otherwise in the domain* $R(x) \geqq \gamma$.

The sufficient condition for the expansion of a function in a binomial-series contained in the above theorem seems, indeed, very simple. If a function $\omega(x)$ can be represented by the equality

$$\omega(x) = (x + b)^k \, c^x \, \mu(x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where c is a fixed number *within* the circle (1,1) and $\mu(x)$ a function remaining within finite limits in $R(x) > \gamma$, then it satisfies the inequality (7) for a value of l differing arbitrarily little from $-\infty$, and therefore it can be expanded in a binomial-series in the domain $R(x) \geqq \gamma$. For $c = 1$ formula (11) gives an expression which shows that all functions regular in the finite part of the half-plane $R(x) \geqq \gamma$ and vanishing at infinity may be expanded as a binomial-series in that domain; further all functions becoming infinitely large at infinity of an order lower than a certain finite power of x; so all irrational and logarithmic expressions.

The way in which we have arrived at our theorem is substantially the same as that followed in the ordinary theory of functions of a complex variable, in order to obtain the expansion of a function in a *power-series*; it is founded upon the fundamental theorem of CAUCHY. According to this we have

$$\omega(x) = \frac{1}{2\pi i} \int_{W} \frac{\omega(z)\, dz}{z - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the integral is taken round a closed curve W, *within* and *upon* which $\omega(x)$ is regular, and which contains the point $z = x$ in its interior. If we wish to deduce from this integral an expansion according to positive integral powers of $x-a$, a being a number

---

1) This series is taken instead of (1) for the sake of generality.

within W, then we start from the *known* expansion with *known remainder* of $1 : (z-x)$ in such a series. In the same way we may reach our present purpose, if we use the *known* expansion with *known remainder* of the just mentioned elementary function in a binomial series, viz.

$$\frac{1}{z-x} = \sum_{0}^{n-1}{}_m \frac{(x-\beta)\ldots(x-\beta-m+1)}{(z-\beta)\ldots(z-\beta-m)} + \frac{(x-\beta)\ldots(x-\beta-n+1)}{(z-\beta)\ldots(z-\beta-n+1)} \cdot \frac{1}{z-x}.$$

Substituting this expression for $1/z-x$ in the integral (12) and choosing the path of integration so as to include, besides the point $z = x$, the points $z = \beta,\ \beta+1, \ldots, \beta+n-1$, we find [1])

$$\omega(x) = \sum_{0}^{n-1}{}_m \binom{x-\beta}{m} \Delta^m \omega(\beta) + R_n \quad . \quad . \quad . \quad (13)$$

where

$$R_n = \frac{1}{2\pi i} \int_W \omega(z) \frac{(x-\beta)\ldots(x-\beta-n+1)}{(z-\beta)\ldots(z-\beta-n+1)} \cdot \frac{dz}{z-x} \quad . \quad . \quad (13')$$

Formula (13) is the ordinary formula of interpolation of NEWTON with a *remainder* added to it and valid for all complex x-values lying within W.

If all points $z = \beta,\ \beta+1, \ldots, \beta+n-1$, are to lie within the integration-curve W, this curve will in general have to be modified with increasing n. It is required to choose W as fit as possible, that is to say: so that the remainder (13') tends to zero with indefinite increase of n, and that yet the aggregate of functions $\omega(x)$ for which this takes place, is as extensive as possible. If, now, the form (7) is taken as majorant-value of these functions, where the number a is, as yet, left undetermined and the number γ, in order to have a definite case, is chosen zero (so that $\beta > 0$), it is found after a rather long but principally not difficult inquirement: 1. that the most favourable integration-curve is a circle with $z = n$ as centre and n as radius so that it passes through the origin; 2. that for a a complex number may be taken lying on the circumference of the circle (1,1), with the specifications concerning the domains of validity already mentioned in the Statement of the above theorem.

We may further observe that, in case the number c in formula

[1]) If a few points $\beta,\ \beta+1, \ldots,$ are *excluded* from the closed curve W, we obtain an expression the further examination of which leads to the so-called *zero-expansions*, which are treated in an elementary way by PINCHERLE (Rendic. d. R. Accad. d. Lincei, 1902, 2e Sem.)

(11) is real and not greater than 1, a *fixed* integration-path W for the remaining integral may be chosen, as soon as the number n attains a certain magnitude, and for this we may take the imaginary axis in this case. The proof that $lim\ R_n = 0$ for $n = \infty$ is then very simple, so that the above mentioned particular cases in which a function can be expanded in a binomial series, may be derived in a *short* manner from CAUCHY's integral.

As further regards the question, how far the inequality (7) is *necessary* for the expansion of a function in a binomial series, the way in which the *sufficient* condition has been obtained gives us the conviction that the aggregate of functions determined by the latter condition is as large as possible. In order to come to certainty concerning this it is necessary to investigate how a function represented by a binomial series behaves in the domain of convergence of that series. This investigation may be effected by means of the statement, contained in the theorem of PINCHERLE, that a binomial series necessarily represents a *coefficientfunction*, at least in the domain of *absolute* convergence of that series, for to this only the proposition of PINCHERLE applies.

For simplicity we assume for the binomial series the original form (1), which is the one considered by PINCHERLE. If the characteristic λ' of the coefficients c_n is less than -1, then, as already mentioned, the binomial series can be represented by the integral (6) in the half-plane $R(x) > 0$. It can now be proved that this integral satisfies, in the domain mentioned, the condition (7), with $\gamma = 0$, the exponent l being subject to the inequality

$$l < -\tfrac{1}{2} + \delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where δ is an arbitrarily small positive number. This condition can further be specified by *extending* a certain property of the operation I by means of which, according to the view of PINCHERLE, the generating function $\varphi(t)$ passes into the coefficient-function $\omega(x)$; we mean the property expressed by the equation

$$I\,[\varphi^{(r)}(t)] = \frac{(-1)^r\,\Gamma(x)}{\Gamma(x-r)}\,I\,[t^{-r}\,\varphi(t)]\,,$$

This equation is given by PINCHERLE (l.c. p. 30) for the case r is a positive integer. If r is replaced by $-\alpha$ and $\varphi(t)$ by $\varphi(t):(t-1)^{\alpha}$, the formula passes into

$$I\left[(-1)^{\alpha}\,D^{-\alpha}\,\frac{\varphi(t)}{(t-1)^{\alpha}}\right] = \frac{\Gamma(x)}{\Gamma(x+\alpha)}\,I\left[\frac{t^{\alpha}\,\varphi(t)}{(t-1)^{\alpha}}\right]. \quad . \quad . \quad (15)$$

The last equation appears indeed to be true for *arbitrary* positive

values of α [1]), if for the derivative of any negative order the definition of RIEMANN is adopted, which in the present case, a neighbourhood of infinity being regarded, can be expressed by the identity

$$(-1)^\alpha D^{-\alpha} \frac{\varphi(t)}{(t-1)^\alpha} = \frac{1}{\Gamma(\alpha)} \int_t^\infty \frac{(u-t)^{\alpha-1}}{(u-1)^\alpha} \varphi(u)\, du \quad . \quad . \quad . \quad (16)$$

Since as domain of t and u the part of the plane *outside* a certain circle with centre (1) is considered, it will be convenient to assume for path of integration between $u = t$ and $u = \infty$ the half-line which has the same direction as the vector from $u = 1$ to $u = t$. The quantities $u - t$ and $u - 1$ then have the same arguments and $(u-t)^\alpha : (u-1)^\alpha$ is real. With these agreements we have the expansion

$$(-1)^\alpha D^{-\alpha} \frac{\varphi(t)}{(t-1)^\alpha} = \sum_0^\infty{}_n \frac{\Gamma(n+1)\, c_n}{\Gamma(n+1+\alpha)\,(t-1)^{n+1}} \quad . \quad . \quad . \quad (17)$$

so that the derivative of negative order $-\alpha$ of the expression $\varphi(t) : (t-1)^\alpha$ is, as $\varphi(t)$ itself, regular and zero at infinity. The characteristic of the derivative is, however, α less and this makes it possible, by means of (15), to express the coefficientfunction $\omega(x)$ of a generating function $\varphi(t)$ with characteristic $\lambda' < -1$ in terms of another generating function $\varphi_1(t)$ whose characteristic is *any small amount* less than -1. The function $\varphi_1(t)$ is constructed in such a way that the given function $\varphi(t)$ is the derivative of a certain negative order $-\alpha$ of $\varphi_1(t) : (t-1)^\alpha$ and the number α is selected from an aggregate of positive values, whose upper limit is equal to the difference between λ' and -1. In other words, if $\varphi(t)$ is given by (3), we take

$$\varphi_1(t) = \sum_0^\infty{}_n \frac{c'_n}{(t-1)^{n+1}}$$

where the meaning of c'_n is given by

$$c_n = \frac{\Gamma(n+1)\, c'_n}{\Gamma(n+1+\alpha)}$$

with

$$\alpha = -1 - \lambda' - \delta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

δ_1 being any small positive number. Then, according to (17)

$$\varphi(t) = (-1)^\alpha D^{\alpha} \frac{\varphi_1(t)}{(t-1)^\alpha}$$

[1]) I have communicated the proof of this truth in the Proceedings of the meeting of September 27, 1919.

and hence by (15)

$$\omega(x) = I[\varphi(t)] = \frac{\Gamma(x)}{\Gamma(x+\alpha)} I\left[\frac{t^\alpha \varphi_1(t)}{(t-1)^\alpha}\right] \quad . \quad . \quad . \quad (19)$$

Not only $\varphi_1(t)$, but also the function

$$\psi(t) = \frac{t^\alpha \varphi_1(t)}{(t-1)^\alpha}$$

has the property that the operation I applied to it gives a coefficient-function satisfying the condition (7), the inequality (14) for l being left unaltered. We only have in this case $\gamma = -\alpha$, instead of $\gamma = 0$, and the domain of validity is determined by $R(x) > -\alpha$, or, according to (18), by

$$R(x) > \lambda + \delta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where

$$\lambda = \lambda' + 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

That is: the domain of validity of (7) is the domain of *absolute* convergence of the series (1) (for δ_1 is arbitrarily small).

For the whole right-hand member of (19), that is for $\omega(x)$ we therefore have the inequality

$$|\omega(x)| < M |(x+b)^l a^{x-(\lambda+\delta_1)}| \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where l, now, satisfies the condition

$$l < \lambda - \tfrac{1}{2} + \delta_1 + \delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

If, at last, the characteristic λ' of $\varphi(t)$ is greater than -1 or equal to -1, then, after PINCHERLE, the coefficientfunction can be expressed in terms of that of another generating function $\varphi_1(t)$, with a characteristic less than -1. First, let

$$-1 \leqq \lambda' < 0,$$

then PINCHERLE considers the additional function

$$\varphi_1(t) = -D^{-1}\left(\frac{\varphi(t)}{t-1}\right),$$

having a characteristic $\lambda' - 1$, which, therefore, is less than -1, so that the corresponding coefficient-function $\omega_1(x)$ satisfies, in the domain $R(x) > \lambda - 1 + \delta_1$, the inequality

$$|\omega_1(x)| < M |(x+b)^l a^{x-(\lambda-1+\delta_1)}|$$

with

$$l < \lambda - \tfrac{3}{2} + \delta_1 + \delta$$

The coefficientfunction $\omega(x)$ of $\varphi(t)$ is connected with the latter by the formula[1])

$$\omega(x) = \Delta[(x-1)\omega_1(x-1)]$$

[1]) PINCHERLE, l. c., p. 64.

from which it follows that $\omega(x)$, precisely in the domain (20), satisfies the inequality (22) with, for l, the inequality (23). In this manner we may prove the same inequality for the intervals $(0,1)$, $(1,2)\ldots$ of λ' in succession.

If $\omega(x)$ satisfies the inequality (22) for a certain value of l, then, evidently, for all greater values. Thus there is a lower limit l_0 for all such values, but this may possibly not be substituted for l in (22). Instead of this we may however write

$$\omega(x) \sim (x+b)^{l_0} a^{x-(\lambda+\delta_1)} \quad \ldots\ldots\ldots \quad (24)$$

with the meaning that (22) holds for any $l > l_0$; we may call (24) an equation of *equivalence* and say that $\omega(x)$ is *equivalent* to the right-hand member of this equation. The exponent l_0 satisfies the condition

$$l_0 \leqq \lambda - \tfrac{1}{2} \quad \ldots\ldots\ldots \quad (25)$$

since δ and δ_1 were arbitrarily small. The proposition relating to the *necessary* condition for a function to be expanded in a binomial-series may thus be expressed in the following manner:

A binomial series of the form (1) *represents in any half-plane* $R(x) \geqq \lambda + \delta$, *differing arbitrarily little from its domain* $R(x) \geqq \lambda$, *of absolute convergence, a function* $\omega(x)$, *which satisfies the equation of equivalence* (24); *the exponent* l_0 *satisfies the inequality* (25).

If, now, this proposition is compared with that relating to the *sufficient* condition, then, to begin with, we find a complete accord between the majorant values (7) and (22). *These majorant-values are, therefore, both necessary and sufficient.* Further, as regards the domains of validity, the inequality (9) here becomes $R(x) > l + \frac{1}{2}$, since we had $\beta = 1$, or we may also write

$$R(x) > l_0 + \tfrac{1}{2},$$

if l_0 is again the lower limit of the l-values which may be taken for the given function. From (25) the same inequality follows with regard to the domain of *absolute* convergence. Since the domain of possibly *conditional* convergence extends at most over a strip of unity-breadth on the left of the domain of absolute convergence, the investigation performed by us leaves room for the possibility that a binomial series sometimes represents a function satisfying the condition (24) also in a strip determined by

$$l_0 - \tfrac{1}{2} < R(x) < l_0 + \tfrac{1}{2}$$

or in a certain part of it. In order to come to certainty concerning this point, we should have to examine how a function represented by a binomial series behaves in the domain of conditional convergence of that series. To such an investigation we have as yet

not arrived; but we may already perceive that the result could not fill up the gap which, as regards the domains of validity, exists as yet between the necessary and the sufficient condition. First: if a function $\omega(x)$ satisfies the equation of equivalence (24) for a *fixed* value of a on the circle (1,1) and for a certain minimum-exponent l_0, then, on account of what has been remarked on the expression $a^{x-\gamma}$, immediately after formula (10), that function satisfies the same inequality, when the number a *varies*, in the specified mode, together with the argument ψ of x. The index l_0 cannot, however, be diminished, because it must at all events be taken for $\psi = -\alpha$, if α is the argument of the original *fixed* number a. The statement belonging to the inequality (9′) informs us, however, that in this case expansion of $\omega(x)$ in a binomial series is possible for $R(x) > l_0$. The function

$$2^x = \sum_0^\infty {}_n \binom{x-1}{n},$$

for which we have $a = 2$, $l_0 = 0$, affords an illustration of this fact, for the expansion is really valid for $R(x) > 0$, and it is *conditionally* convergent for $R(x) \leqq 1$. Therefore we can never find $R(x) > l_0 + \frac{1}{2}$ as a *necessary* condition whereas our theorem concerning the *sufficient* condition only says that expansion is *possible* in the domain defined by the last inequality.

Secondly the last condition only holds in case $\omega(x)$ has no singularities in the finite part of the domain $R(x) > l_0 + \frac{1}{2}$; for otherwise for the latter domain the one must be substituted where $\omega(x)$ is regular and that was defined by the inequality $R(x) > \gamma$.

Thus the proposition regarding the *necessary* condition states that for points in the domain of absolute convergence of the given binomial series we have $R(x) > l_0 + \frac{1}{2}$, but conversely it is not true that in the domain determined by this inequality there is certainly absolute convergence. A simple example is furnished by the function

$$\omega(x) = \frac{1}{x}$$

For this function $l_0 = -\infty$, and yet the function can only in the domain of regularity $R(x) > 0$ be expanded in a binomial series of the form (1).

From these remarks it will be clear that in order to fill up the gap existing as yet between the necessary and sufficient conditions we must give more specified propositions for both conditions. In

other words we should have to succeed in dividing the functional aggregate of all functions satisfying the equation (24) by *special* characterising properties; and so also the aggregate of binomial series, in such a way that between the two kinds of sub-aggregates there existed a *complete* correspondence, such that functions of some sub-aggregate K could only be expanded in binomial series belonging to the sub-aggregate K and in no others. But the problem to find suchlike characterising properties will perhaps be very difficult, since it is required for it to derive the character of a function from that of the coefficients of the series representing it; a problem which already causes the greatest difficulties when it regards the more known power-series.

Chemistry. — "*Urease and the radiation-theory of enzyme action*", III. By Dr. H. P. BARENDRECHT. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of May 3, 1919).

8. *The influence of other substances on the urease activity.*

The question was raised, whether in these concentrated solutions of urea the H-ion concentration was perhaps lowered also through the slightly alkaline substance urea itself.

The electrometric measurement of the p_H in the 8% phosphate solution showed indeed a distinct increase after addition of 8% urea. It was, however, soon established, that this increase was not due to a shifting of the true reaction to the alkaline side, but to a diminution of both H-ions and OH-ions, or, in other words, to a decreased dissociation of H_2O in these concentrated solutions of urea.

This conclusion was readily arrived at by the following experiments.

The p_H was determined again in 8% phosphate solutions. Then a second time after addition of a small amount of ammonia (1 c.c. of $\frac{1}{10}$ N). For each of these estimations 10 c.c. of 9.6% phosphate was brought with water or diluted ammonia to 12 c.c.

The results obtained are summarised as follows:

p_H in:				
Phosphate + 8% urea	Difference	Phosphate alone	Difference	Phosphate + 1 c.c. NH_3 $\frac{1}{10}$ N
6.79	0.11	6.68	0.03	6.71
6.97	0.08	6.89	0.03	6.92
7.59	0.10	7.49	0.07	7.56
7.93	0.10	7.83	0.18	8.01
8.20	0.10	8.10	0.34	8.44

As will be seen from SÖRENSEN's determinations of p_H in standard phosphate mixtures, the buffer-value of these solutions becomes considerably diminished, when p_H approaches 8. Therefore the same

small quantity of alkali, which will leave a p_H of moderate value practically unchanged, will cause a distinct rise in a p_H of about 8. This is clearly borne out by the results, obtained by the addition of ammonia.

The urea, however, increases the p_H to an equal degree, whatever its original value.

This increase is therefore evidently not due to an alkalinity of urea. A substance, however, which possesses no alkalinity, can only lower the H-ion concentration, if it lowers the OH-ion concentration just as much.

This effect may be expected from all neutral substances, when added in such an amount to the solution, that the concentration of H_2O is appreciably diminished, provided their ionising power is much less than that of water. In such a case the dissociation product $C_H \times C_{OH}$ or, as it is usually called, the dissociation-constant of water k_w will show a diminution.

Similar changes of the dissociation-constant of water have been studied before, for instance by LÖWENHERZ [1]) in a paper on "The influence of the addition of ethyl-alcohol on the electrolytic dissociation of water".

In view of this influence on k_w the study of urease action in solutions, mixed with some alcohol, promised interesting results.

The alcohol, employed in these experiments had been freed from carbonic acid by boiling in a flask, attached to a reflux condenser.

The same 8% phosphate buffer-mixtures and Soja extract were used as before in the determination of m in part 4 of this paper. The amount of alcohol, to be mixed beforehand with the phosphate, was calculated so as to obtain a concentration of 5% in the final solution.

For the sake of comparison the same Soja-meal was used as in the previous experiments. Those beans had been powdered a year ago and the meal had shown already some signs of weakening. Especially in alkaline solution its constancy of activity had been found to be diminished. Therefore in the experiments with high p_H the m of the first stage had to be taken rather than the mean. And this value was multiplied by the ratio of the activities at the same p_H, found formerly and now.

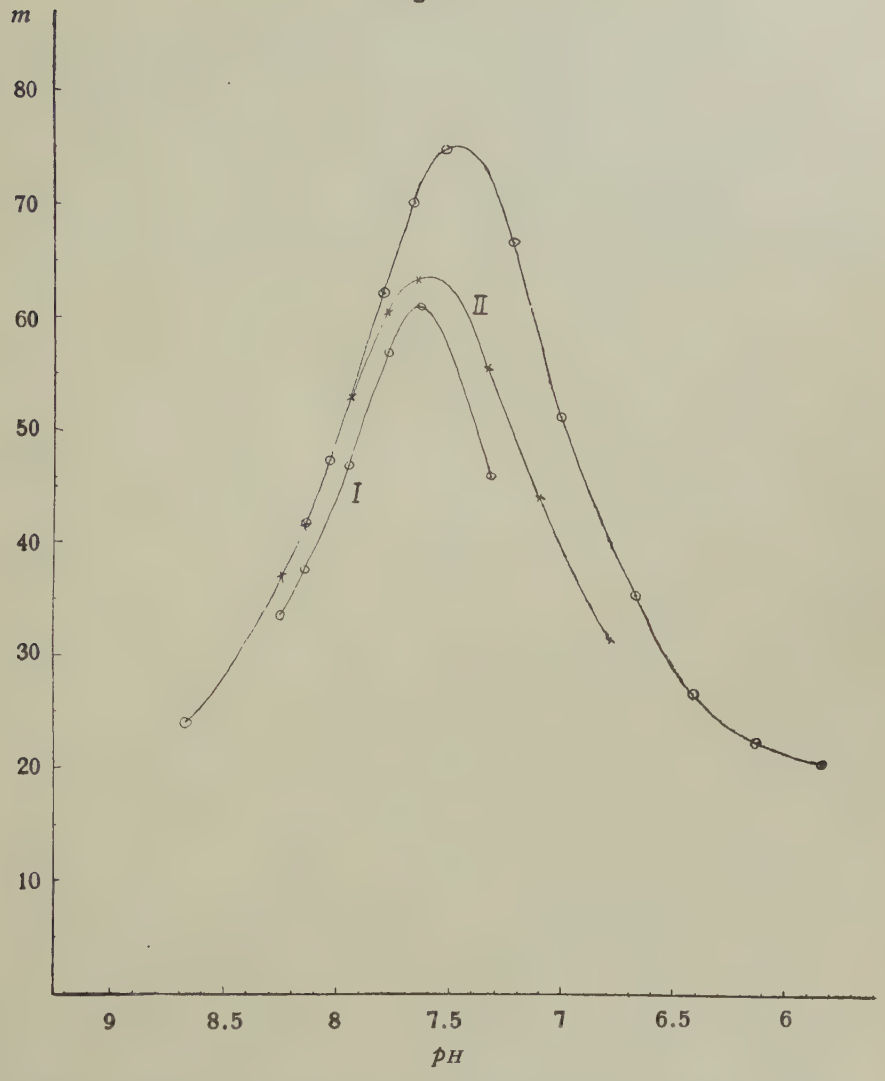
The values, obtained in this way for m in the alcohol solution are plotted in figure 6 *l*, in which for the sake of comparison the original curve for m of fig. 3 is also reproduced.

---

[1]) Zeitschr. physik. Chem. 1896, 20, 283.

The third curve II of this figure has the following meaning:

Figure 6.



According to our interpretation of the rise of p_H of 0,10 by 5 % alcohol, the k_w had increased 0,20, or the p_{OH} 0,10.

As demonstrated in part 5 of this paper m as a function of p_H is:

$$m = 18 + \frac{4828}{1 + \frac{132{,}6 \times 10^{-8}}{(H)} + \frac{2170 \times 10^{-8}}{k_w}(H)}$$

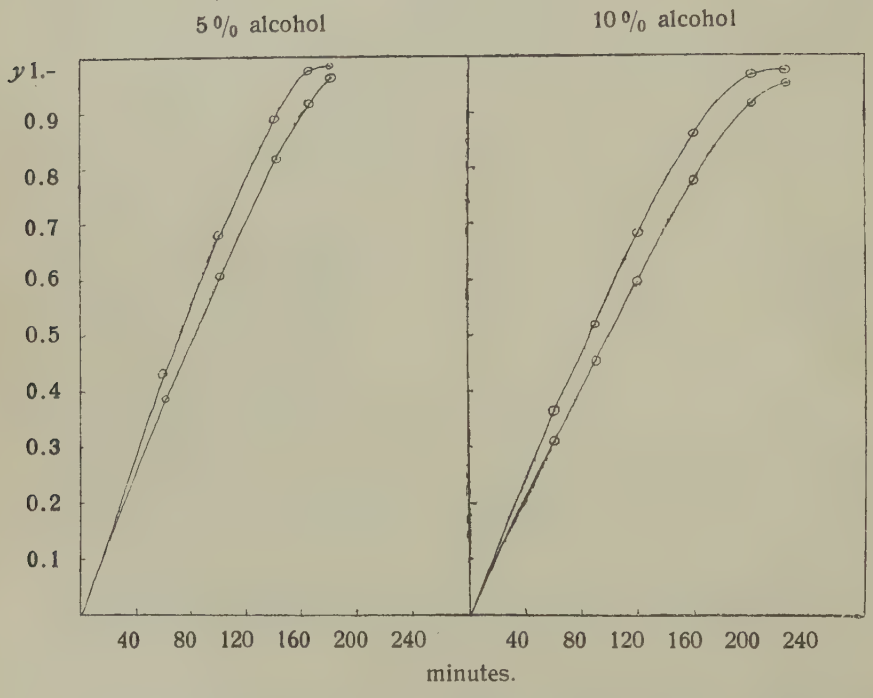
The k_w being diminished by the alcohol from $10^{-13{,}78}$ to $10^{-13{,}98}$, it was now possible to calculate a new curve II for m by means of this formula. The difference between I and II may be due (at

least partly), to the experimental errors, which were very large with the old Soja-meal.

In an earlier stage of these researches the influence of neutral substances like alcohol on urease-action had been studied with the aid of the ammonium-carbonate + carbonic acid as a buffer, in experiments like those described in part 6.

For instance the experiment of May 25th 1916, in which 0,5 % of urea in ammonium carbonate (= 2 % urea) with and without 5 % of alcohol had been investigated, produced the results, represent-

Figure 7.



ed in figure 7. The mean of m without alcohol was 0,00381, with 5 % alcohol 0,00335. For the calculation of m it was assumed, that the p_H had been elevated by 5 % alcohol in this case by the same value as found above in the phosphate solutions.

From figure 6 it will be seen, that between $p_H = 7$ on the original curve and $p_H = 7{,}1$ on curve II, theory would predict a decrease in m from 51,3 to 44,5, that is from 1 to 0,87.

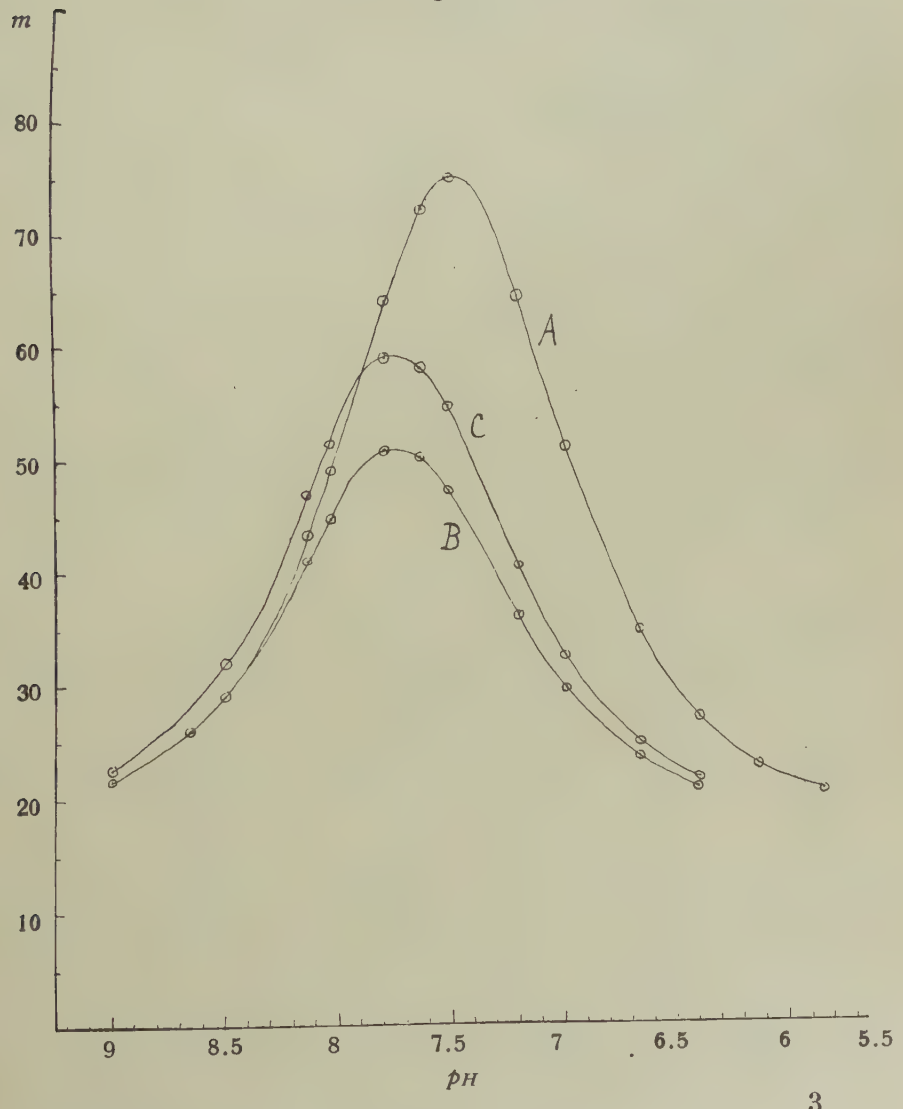
According to the above results a decrease is found from 38,1 to 33,5, that is from 1 to 0,88.

Closer consideration as well as further experimental research showed however, that the problem is more complicated than represented so far.

Alcohol not only diminishes the dissociation constant of water by diminishing the concentration C_{H_2O} in $C_H C_{OH} = kC_{H_2O}$, but, owing to its ionising power being far less than that of water, it will also diminish the dissociation constant of a dissolved electrolyte. Therefore the dissociation constants of the amphoteric electrolyte urease must be expected to be also diminished by alcohol.

The effects of the first influence of alcohol are, as shown in fig. 6, a lowering of the curve and a displacement of the maximum to the left; that of the second one, the diminishing of k_a and k_b at the same rate, is evidently an increase of m, the undissociated fraction, without changing the abscissa of the maximum.

Figure 8.



What we observe is therefore the superposition of a positive and negative effect, the decrease of the dissociation constant of water predominating in this case.

Repetition of the experiment of May 25th 1916, but now with 10 % alcohol, gave on May 30th the result, summarised in figure 7. Without alcohol was found $m = 0{,}00326$, with 10 % alcohol $m = 0{,}00267$.

The electrometric estimation of the p_H in 8 % phosphate solutions with 10 % alcohol had given:

with 10 % alcohol	7,13	7,53
without alcohol	6,89	7,29
difference	0,24	0,24

Thus a constant rise of 0,24, which means a change in k_w from $10^{-13,78}$ to $10^{-14,26}$.

Figure 8 shows, together with the original curve of fig. 1 the curve B, calculated for

$$m = 18 + \frac{4828}{1 + \frac{123.6 \times 10^{-8}}{(H)} + \frac{2170 \times 10^{-8}}{k_w}(H)}$$

with the value $10^{-14,26}$ for k_w.

The results of this calculation are represented by column 3 of the following table.

TABLE 19.

p_H	$10^8 C_{OH}$	m	m (for k_a and k_b 20 % smaller)
8.13	74.13	41	46.8
8.03	58.88	44.8	51.4
7.80	34.67	50.8	59.—
7.64	23.99	50.3	58.3
7.52	18.20	47.4	54.7
7.21	8.90	36.1	40.7
7.—	5.495	29.8	32.7
6.67	2.57	23.7	25.—
6.40	1.38	21.—	21.8
8.5	173.8	29.2	32.—
9.—	1660.—	21.6	22.5

This table and curve B of Fig. 8 would predict a decrease in m from 51.3 for $p_H = 7$ to 37.1 for $p_H = 7{,}24$, that is from 1 to 0.725, whereas according to table 42 experiment produced a decrease from 1 to 0.82.

The interpretation of this difference is, that the k_a and k_b are also appreciably diminished by 10 % alcohol, that therefore the "rest-curve" of urease in this solution has to be placed above the curve B of Fig. 8.

The curve C in Fig. 8 and the fourth column in table 19 represent the values which m would have, if both k_a and k_b had increased by 20 %, k_w having, as in curve B, the value $10^{-14{,}26}$.

Attention may here be drawn to the fact, that if a neutral body like alcohol, diminishes the dissociation constants of urease as well as of water, the new curve for m intersects the original one, which means, that in such a case a considerable decrease of activity is to be expected at low p_H (in the present case below $p_H = 7.85$) and by the same agency, the addition of alcohol, an increase at high p_H.

The influence of neutral salts may be illustrated by the example of 5% KCl.

Here, as in all previous cases, 5 % means 5 gram in 100 c.c. of the reacting solution.

In 8 % phosphate solutions the p_H was found not to be raised, but to be diminished in a constant degree by 5 % KCl.

	p_H		
without KCl	6.13	6.89	7.29
with 5 % KCl	6.00	6.79	7.19
difference	0.13	0.10	0.10

Nevertheless in the ammonium carbonate solution KCl had produced a considerable decrease of urease activity. Without KCl $m = 0{,}0031$, with 5 % KCl $m = 0.0022$.

The conclusion, to be drawn from these facts, is, that a neutral salt like KCl increases all dissociation constants, that of urease as well as that of water.

We thus have here again and in a marked degree, a change in the nature of urease, a general decrease in its activity, brought about by an increase of its dissociation-constants.

The raising of the dissociation-constant of water by salts had already been observed in this study in the determination of the hydroxyl-ion concentration in 8 % phosphate solutions, the dissociation-constant of water having been found to be $10^{-13{,}78}$, instead of $10^{-13{,}825}$, as it is in pure water.

Moreover, the stimulating action of neutral salts on the catalytic activity of hydrogen-ions has long since been attributed to a raising of the dissociation constants of acids by salts.

Another instance of such an effect has recently been supplied by KOLTHOFF [1]), who showed, that the dissociation-constants of indicators are increased by the addition of neutral salts.

Mannitol showed the same behaviour as potassium chloride.

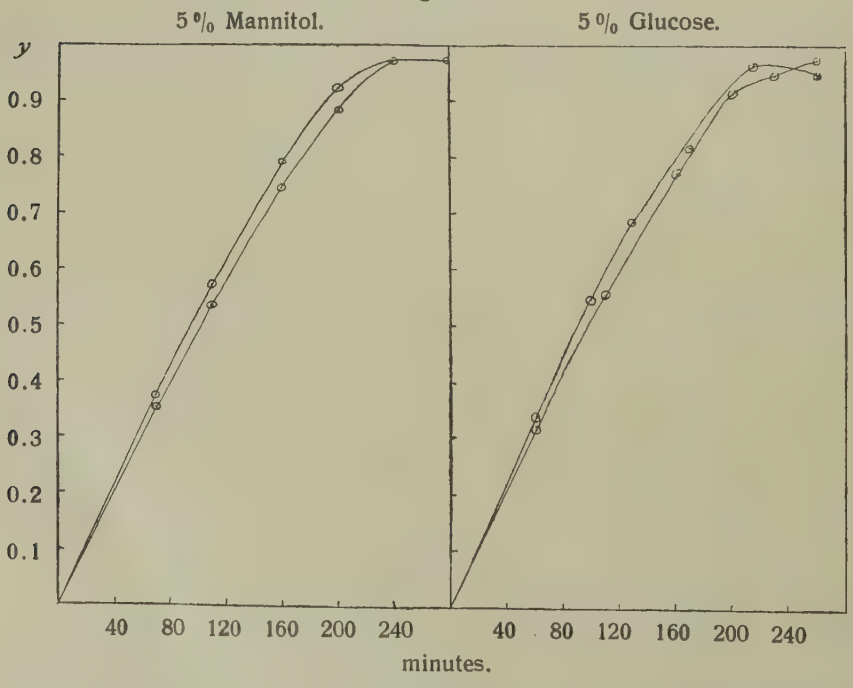
In 8 % phosphate solutions the following values for p_H were determined:

without mannitol	6.89	7.29
with 5 % mannitol	6.84	7.24
difference	0.05	0.05

Hence again a constant decrease of p_H, that is an increase of the dissociation-constant of water.

In ammonium carbonate solution 5 % mannitol produced a small decrease of urease activity (m decreased from 0.0029 to 0.00275), from which it is to be inferred, that the dissociation-constants of urease are increased by this neutral substance also.

Figure 9.



Glucose, added to the amount of 5 % to ammonium-carbonate

[1]) Chem. Weekblad 1918, 394.

solution, gave only rise to a very slight decrease of urease activity. The cases of mannitol and glucose are illustrated by fig. 9.

It will be seen, that the general nature of the curves is not changed by the addition of neutral substances, from which it can be inferred, that only the m in our fundamental formula

$$-dx = m \frac{x}{x + nc} dt$$

is affected.

If other substances absorbed the radiation like the hydrogen-ions, the shape of the curves would have been altered, tending with progressive change to the logarithmic curve.

The facts recorded above and the theoretical deductions might afford some explanation of at least a part of ONODERA's observations [1]), that alcohols can increase as well as decrease the action of urease. The experiments of this author, however, were made without buffer-mixtures and without any estimations of the p_H, which in the absence of buffers must have varied enormously. Since the long duration of urease action in those undefined, but certainly rather alkaline, conditions, must have had a deteriorating influence on the urease, the more so, the higher the p_H, a neat interpretation of these results is rendered impossible.

9. *Reversion of the hydrolytic action of urease on urea.*

The generally accepted view of the synthetic action of enzymes, shared also by the present author, is, that one and the same enzyme is the active agent in breaking down as well as in building up its specific substrate.

The conditions, however, which cause either of the two opposite activities to predominate, have as yet not been made clear.

Some observations, made in the course of this study and a general consideration of the enzyme activity in living tissues, induced the writer to venture the following hypothesis:

Around an enzyme particle the substrate is broken down as long as the action, radiating from the enzyme, is vigorous enough. Weakened by spreading or by other causes, the same enzyme radiation produces the reverse process, synthesis.

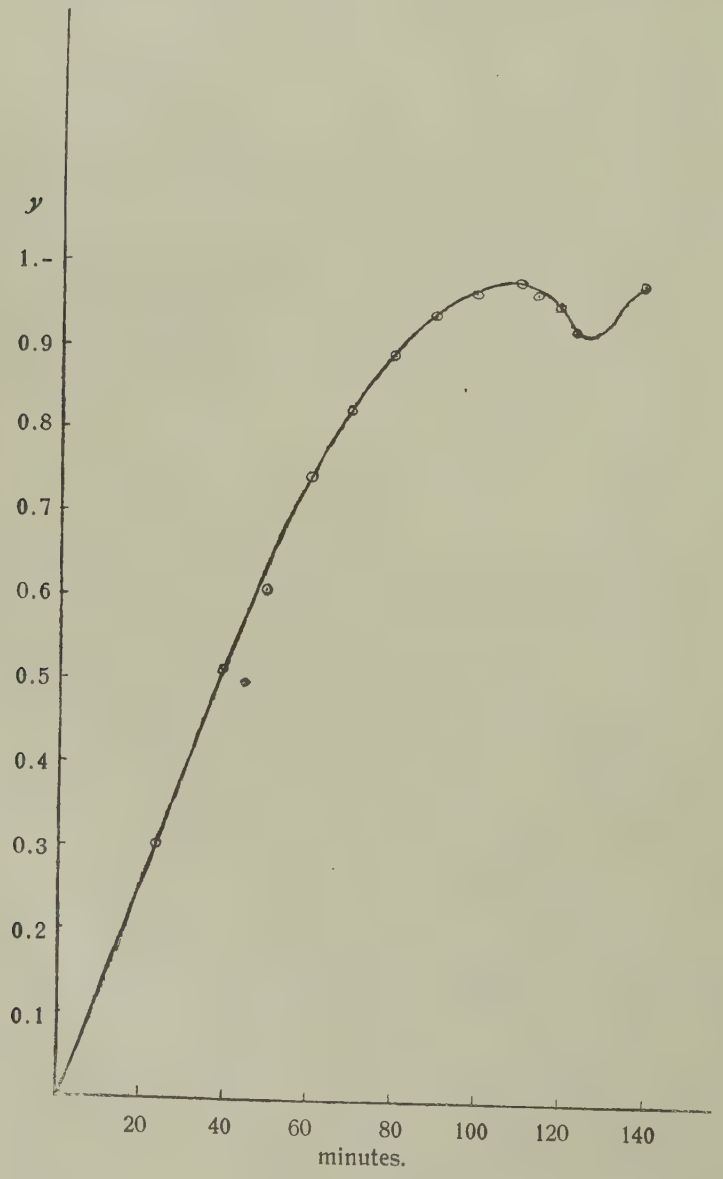
In the living plant and animal both activities of the enzyme are going on continuously under ordinary conditions as to concentration of substrate, temperature and acidity. As soon, however, as the tissue,

[1]) Biochem. J. 1915, 563.

by extraction and pulverisation, is made into a homogeneous mixture or solution, nearly all synthetic power of the enzyme disappears.

As is well known, in order to extract say glucosides from plants, it is necessary first to destroy the enzymes by boiling the seeds or the leaves, before the cells are broken up for extraction. The glucoside and its enzyme are, as demonstrated already by GUIGNARD, located in different adjoining cells. The hypothesis that enzymes display their synthetic effect only at a certain distance, affords at once an explanation of these facts. Through the cellwalls the radiation

Figure 10.



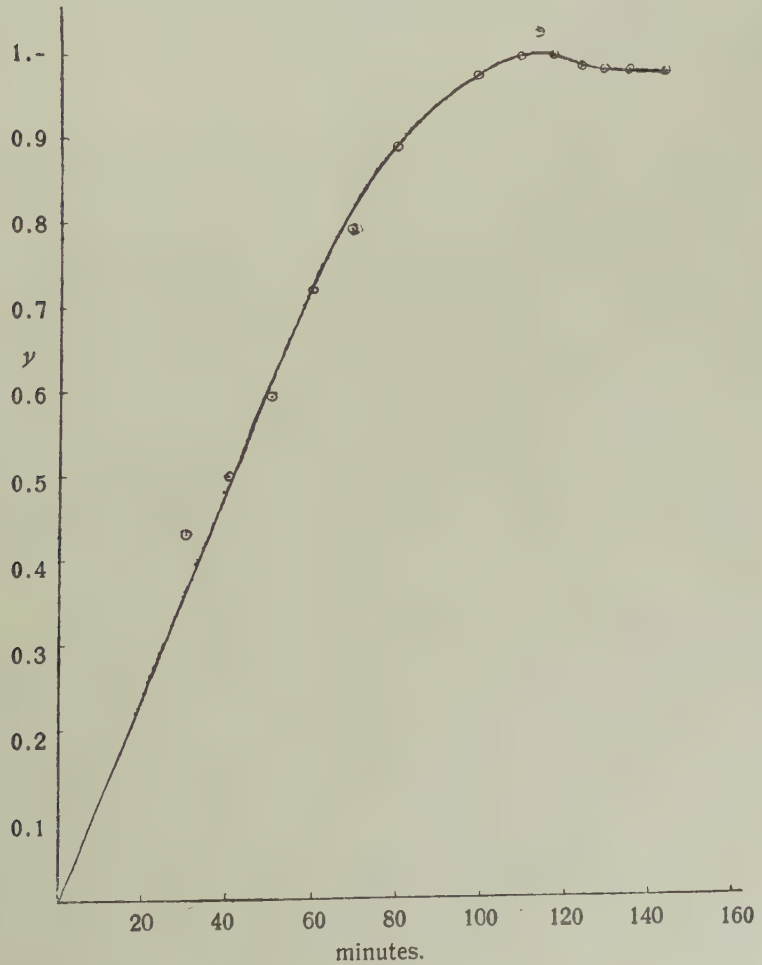
causes synthesis in the neighbouring cells; as soon as enzyme and substrate are brought together, the hydrolytic action prevails almost exclusively.

This conception of enzyme activity is borne out by experiment in different ways.

The weakening of the radiation may be occasioned, as observed above, not only by spreading, but also by other factors, e.g. by the deteriorating action of temperature and acids or alcalis in a shorter or longer time. As will be seen, in what follows, several times a reversion of the hydrolysis of urea was observed, which could be explained by a decay of the urease.

Nov. 18th 1915 an experiment was carried out with ammonium-carbonate as a buffer, in which this reversion at the end of the hydrolysis manifested itself clearly. See figure 10, p. 10.

Figure 11.



It is to be expected, that the enzyme molecules will not all decay at the same time. At the end of the hydrolysis, when the action on the rest of the urea has become very slow, and on the other hand the concentration of the reaction products has grown correspondingly, it may happen, that a sufficient proportion of the enzyme particles is in the decaying state to cause the synthetic action, having a higher concentration of substrate at its disposal, to predominate over the slow action of the unchanged enzyme on the relatively very diluted urea solution. During such a period the total effect will be reversed, returning to its normal course as soon as the unchanged enzyme particles prevail over the decaying ones, which may be occasioned by a further weakening or total decay.

Figure 11 shows the results of an experiment of Jan. 2nd 1916, like that of Nov. 28th, 1915, which shows the same phenomenon in a smaller degree.

In the phosphate solutions of high p_H also the reversion sometimes became manifest.

First a regular experiment of April 6th, 1917 may be recorded.

TABLE 20.

0.25 gr. Soja + 50 c.c. water + 3.64 gr. Na_2HPO_4 2 aq. + 1.16 gr. KH_2PO_4
10 c.c. filtrate mixed with 11.52 gr. Na_2HPO_4 2 aq. + 120 c.c. water.

$p_H = 8.13$ 0.01 % urea

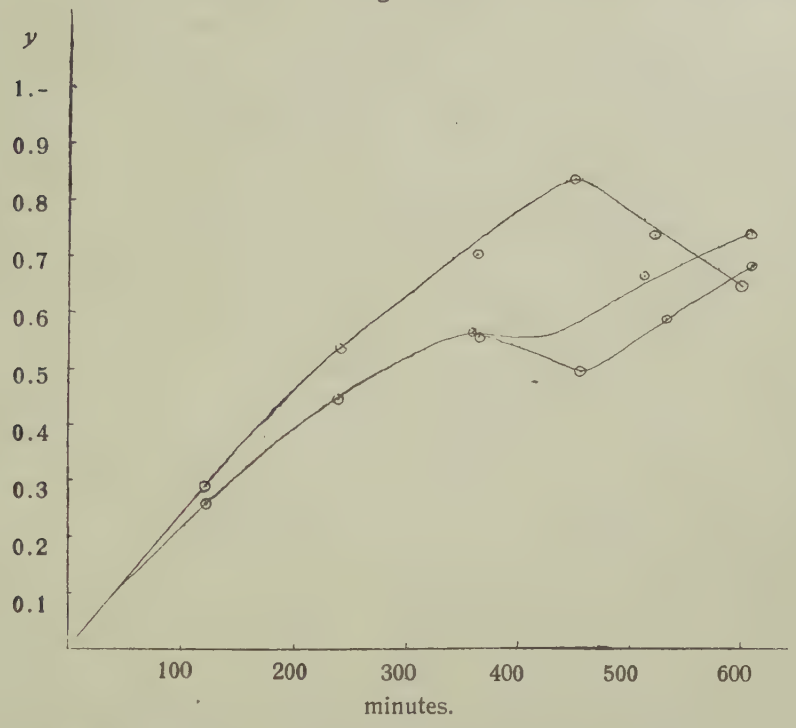
t (minutes)	y	$m = \frac{0.0073 \log \frac{1}{1-y} + 0.01y}{t}$
80	0.17	0.000029
140	0.305	0.000030
200	0.39	0.000027
260	0.52	0.000028
321	0.625	0.000030

In this case little or no destruction had taken place during this interval; for 10 c.c. of the extract, left alone for 320 minutes in the same bath at 27° and then mixed with 2 c.c. urea (0.06 %) gave in 80 minutes 0.3 c.c. NH_3 $\frac{1}{50}$ N, which makes $m = 0.000026$.

April 10th 1917. The same arrangement as on April 6th but now with longer time intervals. Part of the same mixture left in the bath at 27° till the next day, when 10 c.c. with 2 c.c. urea solution of 0.06 % gave in 260 minutes only $y = 0.1$ (against y about 0.45 originally). Thus evidently a considerable decay of the enzyme had taken place.

April 16th and 23rd 1917. A repetition of the experiment of April 10th. The results of these three experiments are represented

Figure 12.



in fig. 12. As will be seen clearly in the curves of April 10th and 27th, there is first a decline, after which the reaction proceeds normally again. As discussed above the inference of this is, that during some time interval the decaying enzyme particles, which cause the synthesis, may prevail, and that after their total decay (or perhaps restoration) the normal enzyme action sets in again.

In order to test this conception more directly the following experiment was carried out.

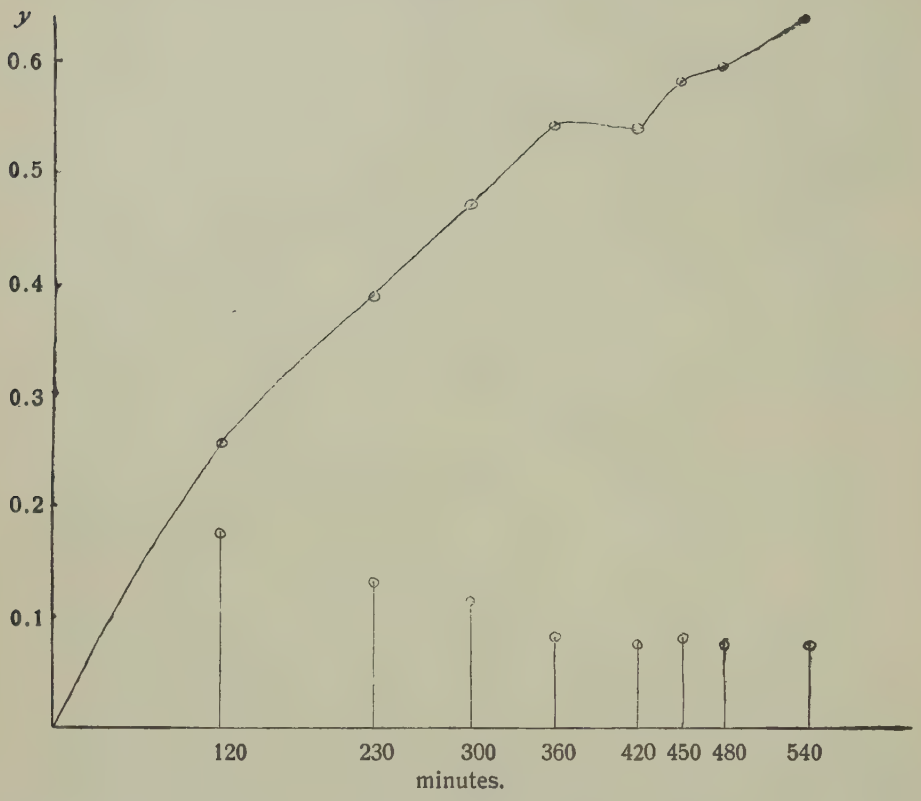
In one row of tubes the rate of hydrolysis of an 0.01 % urea solution in 8 % phosphate of $p_H = 8.13$ was investigated as before.

Another row of tubes, each also with 10 c.c. of the same Soja-extract-phosphate-solution had been placed with all the other tubes at the same time in the same bath of 27°. Immediately after taking out a tube of the first row for analysis, 2 c.c. urea solution of 0.06% were introduced into a tube of the second row and the reaction in this one allowed to proceed for 120 minutes. In this way it was possible to get some information about the rate of decay of the enzyme.

From Fig. 13 it will be seen, that the nearly horizontal part of

the curve coïncides with the T's of diminishing activity according to table 21. Between $T = 120$ and $T = 230$ there seems to have

Figure 13.



been in the beginning another period of some decay, followed by a normal course from $T = 230$ to $T = 360$.

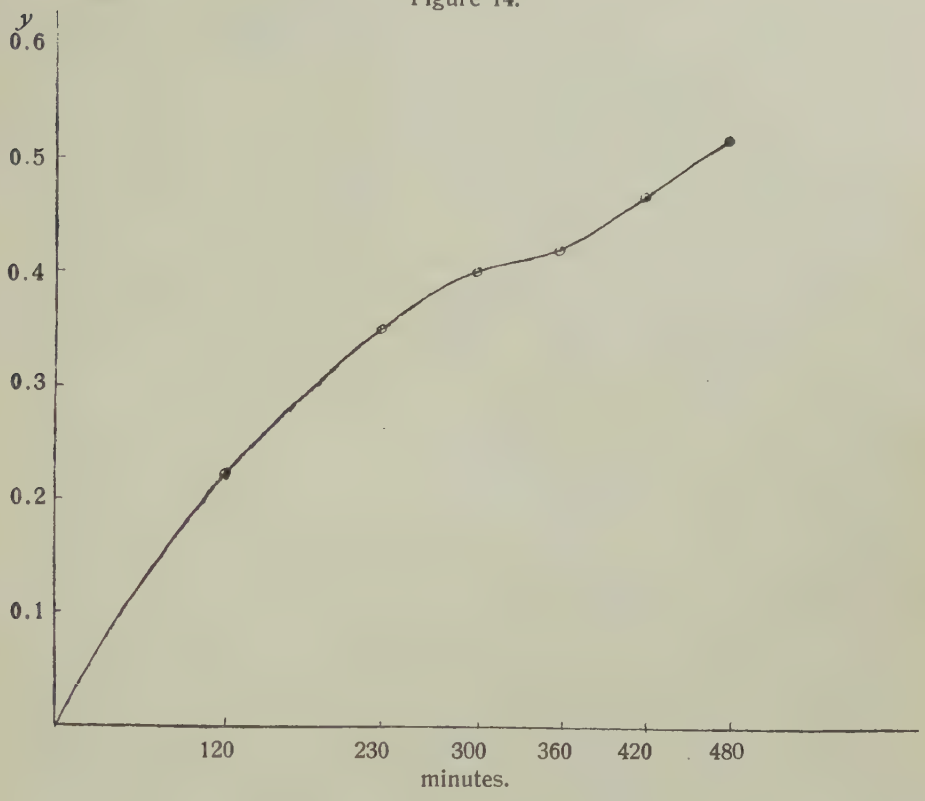
This peculiar type of curve, first a retardation and then again

TABLE 21.

T (minutes)	y	y (in 120 minutes after the time T)
120	0.255	0.175
230	0.385	0.130
300	0.465	0.115
360	0.535	0.08
420	0.53	0.075
450	0.575	0.08
480	0.585	0.075
540	0.625	0.075

a normal slope, was observed more than once on repeating the same experiment at $p_H = 8.13$. For instance on July 19th., 1917. Fig. 14.

Figure 14.



10. *Influence of the concentration of enzyme.*

In continuing the investigations of part 4 with smaller enzyme-concentrations it was first observed, that in the same conditions the same quantity of Soja-meal did not always give the same result. In preparing the necessary solutions the distilled water had been freed from carbonic acid by boiling in a tin coated copper flask. After this method of purifying the distilled water had been replaced by distilling the water once more in a Jena flask and glass condenser, rejecting the first part of the distillate, more regularity seemed to be obtained. Still, weighed off in such small amounts, the Soja-meal appeared to be not quite homogeneous. An explanation of this fact will be brought forward further on.

Nevertheless important new results could be obtained in this way.

For the sake of the necessary constancy of p_H the urea-concentration in these experiments was again 0,01 %.

Taking the same unit as before the concentration of the urease was now $\frac{3}{256}$.

Twice also a series of four experiments with different p_H was made simultaneously with the same Soja extract to make sure, that in all the same quantity of enzyme had been brought into solution.

Evidently the smallness of enzyme concentration involved the necessity of long reaction-time.

In order to investigate, if during such long exposures to these H-ion concentrations at 27° any weakening of the enzyme activity had taken place, the remaining parts of the four phosphate-enzyme-solutions were left for 24 hours in the bath at 27°. On the next day the required experiments were repeated with these ones.

In this way it became manifest, that the combined action of H-ion concentration, temperature and time had here, within the limits of experimental errors, no appreciable effect on urease in the acid solutions. If, however, at 27° the H-ion concentration was maintained beyond the neutral point, the activity of the enzyme decreased slowly, but distinctly. In alkaline solutions for the calculation of m, as before, only the measurements of the first intervals had to be used.

The acidity, used in these experiments, had itself no hydrolytic action on urea, as was ascertained by boiling samples of 10 c.c. of the liquids with $p_H = 6{,}67$ and $p_H = 7{,}52$, incubating them for 24 hours at 27°, adding to each 2 c.c. of 0,06 % urea and maintaining these mixtures again for 24 hours at 27°. No ammonia was formed.

The results obtained for the specific urease-activity m of low urease concentrations are brought together in fig. 15, in which for the sake of comparison the curve of fig. 3 is also reproduced.

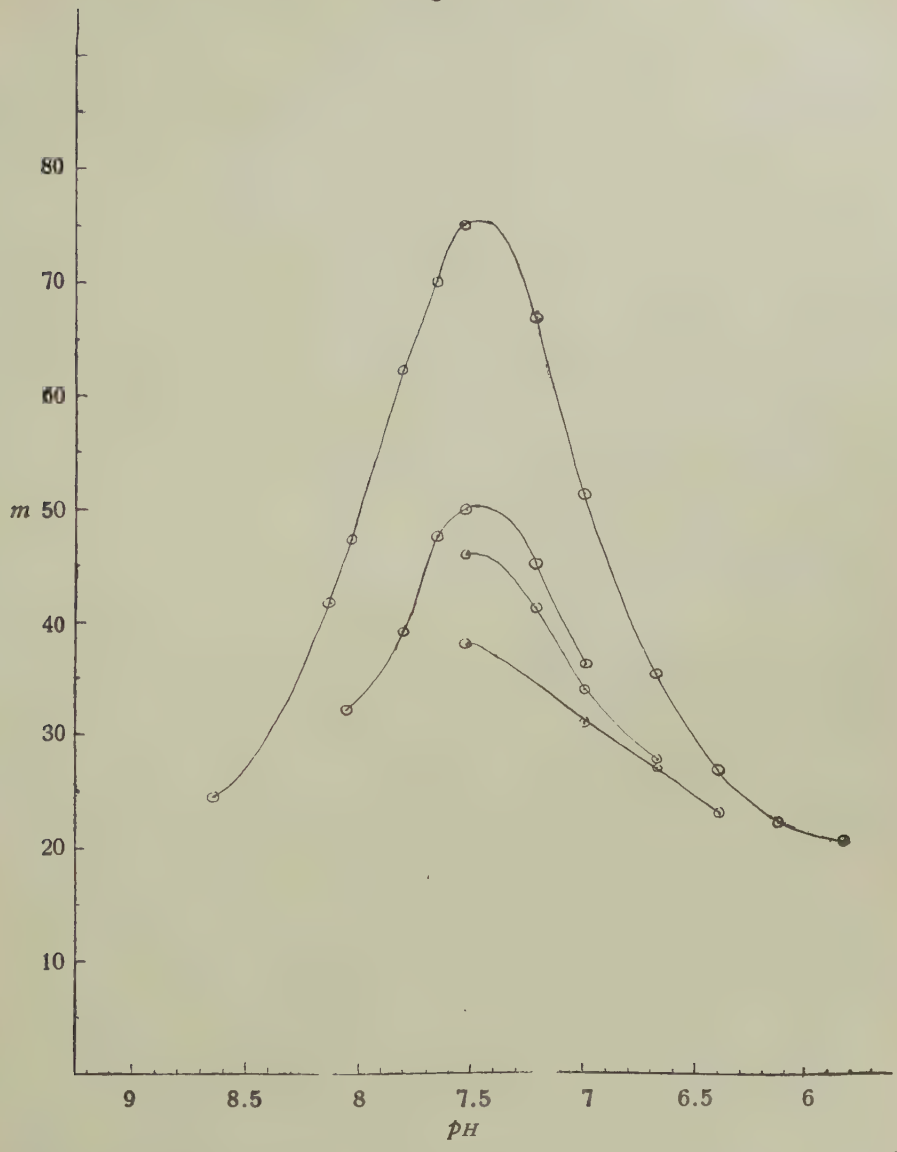
The interpretation of these results, based on the theory, put forward in part 9 is the following.

An enzyme molecule being the centre of two concentric spheres, an inner one, in which the substrate is broken down, and an outer shell, in which the reverse action is brought about, it is evident, that, if the concentration of the enzyme is large enough to make the inner spheres intersect each other, there is no place in the solution, where the condition for synthesis, that is weakened radiation, is realised; at least, so long as the enzyme has retained its original activity.

A sufficient dilution of the urease will, however, establish a distance between the enzyme-molecules, large enough, to leave the outer shell open for the reverse action. The total power of urease to convert urea into ammonium carbonate, representing the difference between the hydrolysis and the synthesis it brings about, must therefore be expected to be diminished by decreasing the urease concentration beyond a certain value.

The observed facts are clearly in accordance with this theory:

Figure 15.



above a certain value of urease concentration constancy of specific activity, below it a decrease.

The peculiarity, mentioned in the beginning of this part, that small concentrations of urease showed less constancy of power than larger ones, becomes now not only intelligible, but even adduces evidence to the theory.

For, evidently, in regions, where the specific activity is falling off, a slight change in concentration of the urease will have far more effect than at higher concentrations, where the specific activity is constant.

To be continued.

Mathematics. — *"A general definition of limit with application to limit-theorems"* [1]). By Prof. FRED. SCHUH. (Communicated by Prof. J. CARDINAAL).

(Communicated in the meeting of May 3, 1919).

1. Let us assume an aggregate V of real or complex numbers, in which the same number may occur repeatedly. This can take place, if a mode of arising of the numbers of V has been given and various modes of arising may lead to the same number. Those equal numbers however, are considered as different elements of V, so that we distinguish between a number having arisen in the former and the same number having arisen in the latter manner.

2. Next we assume a law given *by which every positive number* δ *is made to correspond to a part* V_δ *(consisting of at least one element) of* V (covering of the aggregate of the positive numbers by the aggregate of the parts of V), in this way, *that* $V_{\delta'}$ *is a part of* V_δ, *if* $\delta' < \delta$; here V_δ is called a part of V if each element of V_δ is an element of V, so that the part can be identical with the whole aggegrate. If now L is a (real or complex) number with the property *that corresponding to every positive number* δ *there exists such a positive number* ε *that every element* E *of* V_δ *satisfies the inequality* $|E-L| < \varepsilon$, then L is called the LIMIT *of the aggregate* V *as regards the covering by which* V_δ *is made to correspond to* δ. It is clear that there can be at most but one number with the beforementioned property.

3. The covering observed in n°. 2 we call EQUIVALENT to a second covering by which a positive number δ is made to correspond to a part V'_δ of V, *if corresponding to every positive number* δ *a positive number* δ_1 *can be found so that* V'_{δ_1} *is a part of* V_δ *and* V_{δ_1} *is a part of* V'_δ. It is evident *that this equivalence is a transitive one.* It furthermore easily appears *that two equivalent coverings both give the same limit, or no limit exists in the two cases.* Hence equivalent coverings can be considered as the same limittransition, so that with a MANNER OF LIMITTRANSITION we mean a *set of mutually equivalent coverings of the kind mentioned in* n°. 2.

4. *The limit defined in* n°. 2 *exists, and exists only then, if corre-*

[1]) For further particulars c.f. Hand. van het Nat. en Geneeskundig Congres 1919.

sponding to every positive number ε *a positive number* δ *can be found so that every pair of elements* E *and* E' *of* V_δ *satisfies the inequality* $|E-E'| < \varepsilon$ (GENERAL PRINCIPLE OF CONVERGENCE). That this condition is *necessary* for the existence of a limit is obvious.

That this condition moreover is *sufficient*, appears in the case of real numbers by noticing that (the condition being fulfilled) a number satisfying the definition of a limit is furnished by the upper boundary of the numbers a, for which there exists a V_δ, all elements of which are $> a$. In the case of complex numbers the theorem is further proved by applying the theorem for real numbers to the real parts and the coefficients of i of the complex nnmbers.

5. Let V and W be two aggregates of numbers, the elements of which being placed into correspondence. We suppose the coverings of the positive numbers by the aggregates of the parts of V resp. W to be of such a nature, that for each positive number δ the parts V_δ and W_δ in the correspondence between V and W are corresponding ones.

We now form an aggregate U by adding the corresponding elements of V and W, at the same time transferring the covering to U. *If now with these coverings* V *shows a limit* L_v *and* W *a limit* L_w, *then also* U *has a limit, viz.* $L_v + L_w$, as may easily may be deduced from the definition of limit.

Other known limit-theorems also can be stated in this manner in a general way.

6. We now suppose, that the elements of the aggregate V are *real* numbers. About the existence however of a limit of V, as regards the chosen covering, nothing is assumed to be known. We can then consider the *lower boundary of the upper boundaries of the aggregates* V_δ, and call it the UPPER LIMIT *of the aggregate* V *as regards the considered covering*. The upper limit B is $+\infty$, if all aggregates V_δ are unbounded to the right, and $-\infty$, if the aggregate of the upper boundaries of the aggregates V_δ is unbounded to the left.

We likewise call the *upper boundary* O *of the lower boundaries of the aggregates* V_δ the LOWER LIMIT *of* V *as regards the considered covering*; this lower limit can also be $\pm\infty$. It is easily proved, *that* B *and* O *always satisfy the inequality* $O \leqq B$.

The aggregate V has a limit L then only, when O and B are equal and finite; we then have $L = O = B$. If O and B are both $+\infty$, we speak of an IMPROPER LIMIT $+\infty$, if O and B are both $-\infty$, of an IMPROPER LIMIT $-\infty$.

Mathematics. — *"A general definition of uniform convergence with application to the commutativity of limits"*. By Prof. FRED. SCHUH. (Communicated by Prof. CARDINAAL).

(Communicated in the meeting of May 3, 1919).

1. Let us assume *two aggregates V and W with coverings of the positive numbers by the parts of V resp. W*, as described in my paper "A general definition of limit", p. 46. By these coverings to a positive number δ a part V_δ of V and a part W_δ of W is made to correspond in such a way, *that V_δ and W_δ contain at least one element, $V_{\delta'}$ being a part of V_δ and $W_{\delta'}$ a part of W_δ if $\delta' < \delta$.*

Let VW be the *productaggregate*, whose elements are formed by combining an element of V with an element of W into a pair (disregarding sequence). The covering by the parts of VW is taken such, *that the aggregate $V_\delta W_\delta$ corresponds to δ.*

If we replace the coverings belonging to V and W by equivalent ones (c.f. n°. 3 of my previous paper) the covering belonging to VW is likewise replaced by one equivalent to it.

2. We assume *VW covered with (real or complex) numbers*, so that every element of VW is made to correspond to a number. From this arises an aggregate K of numbers, in which the same number may occur several times. We shall indicate by G an *aggregate of elements of K, corresponding to a same element of V*, combined with all elements of W. There likewise arises an aggregate H *by considering a constant element of W.*

The covering by the parts of VW can be transferred to the aggregate K. Likewise the covering by the parts of V or W is to be transferred to every aggregate H resp. G.

3. Suppose that every aggregate G (as regards the covering by the parts of W) possesses a limit L_G; then corresponding to every element of V there exists a number L_G. We say, *that the aggregates G converge* UNIFORMLY *to their limits L_G*, if corresponding to every positive number ε there exists such a positive number δ, that each element E of the part G_δ of G satisfies the inequality $|E - L_G| < \varepsilon$, whichever element of V (hence whichever aggregate G) we may choose; it being required, *that δ is independent of the chosen element of V.*

From the general principle of convergence (c.f. n°. 4 of my previous paper) it follows, that uniform convergence exists then and then only, if corresponding to every positive number ε a positive number δ independent of G can be found, so that every two elements E and E' of G_δ satisfy the inequality $|E-E'|<\varepsilon$.

4. Let it now be assumed, *that the uniform convergence mentioned in n°. 3 does exist* and moreover, *that every aggregate H has a limit L_H as regards the covering by the parts of V*; in consequence of this there is a number L_H corresponding to every element of W.

We now first demonstrate, *that the aggregate $\{L_G\}$ of the numbers L_G possesses a limit L as regards the covering by the parts of V.* For this purpose we must prove, that corresponding to every positive number ε such a V_δ can be found, that every two elements of V_δ satisfy the inequality $|L_G - L_{G'}|<\varepsilon$, where L_G and $L_{G'}$ are the numbers of $\{L_G\}$ corresponding to these elements. If E and E' are elements of G resp. G', belonging to a same aggregate H, we have:

$$|L_G-L_{G'}|\leqq|L_G-E|+|E-E'|+|E'-L_{G'}|.$$

On account of the uniform convergence of the aggregates G the aggregate H can be chosen thus, that $|L_G-E|$ and $|E'-L_{G'}|$ are both $<\frac{1}{3}\varepsilon$. As H possesses a limit, we can choose δ thus, that every two elements E and E' of H_δ satisfy the inequality $|E-E'|<\frac{1}{3}\varepsilon$. For the numbers L_G and $L_{G'}$ corresponding to two elements of V_δ then $|L_G-L_{G'}|<\frac{1}{3}\varepsilon+\frac{1}{3}\varepsilon+\frac{1}{3}\varepsilon=\varepsilon$ holds good.

5. We next prove, *that the aggregate $\{L_H\}$ of the numbers L_H (as regards the covering by the parts of W) likewise has the limit L.* We therefore proceed from

$$|L_H-L|\leqq|L_H-E|+|E-L_G|+|L_G-L|,$$

in which E is the common element of the aggregates G and H. On account of the uniform convergence mentioned in n°. 3 we can determine the positive number δ in such a way, that $|E-L_G|<\frac{1}{3}\varepsilon$ holds good if E be an element of G_δ, i.e. if H corresponds to an element of W_δ; here ε is an arbitrarily chosen positive number. If we have now chosen a determinate element of W_δ (by which also H and L_H are determined), we can find the positive number δ_1 in such a way, that the inequality $|L_H-E|<\frac{1}{3}\varepsilon$ is satisfied, if E be an element of H_{δ_1}, i. e. corresponds to an element of V_{δ_1}. Further we can determine δ_2 thus, that we get $|L_G-L|<\frac{1}{3}\varepsilon$, if G corresponds to an element of V_{δ_2}. By making the aggregate G to

correspond to a common element of V_{δ_1} and V_{δ_2}, we obtain $|L_H - L| < \frac{1}{3}\varepsilon + \frac{1}{3}\varepsilon + \frac{1}{3}\varepsilon = \varepsilon$ for every aggregate H corresponding to an element of W_δ.

6. Finally we prove, *that the aggregate K (as regards the covering by the parts of VW) likewise has the limit L.* We obtain:

$$|E - L| \leqq |E - L_G| + |L_G - L|,$$

E being an element of G. Owing to the uniform convergence the positive number δ_1 can be determined so, as to give $|E - L_G| < \frac{1}{2}\varepsilon$ if E be an element of G_{δ_1}, i. e. corresponds to an element of W_{δ_1}. At the same time we can δ_2 determine so, as to obtain $|L_G - L| < \frac{1}{2}\varepsilon$ if G corresponds to an element of V_{δ_2}. If now δ be the smallest of the numbers δ_1 and δ_2, then the inequality $|E - L| < \frac{1}{2}\varepsilon + \frac{1}{2}\varepsilon = \varepsilon$ is satisfied, if E corresponds to an element of V_δ and to an element of W_δ (hence to an element of $V_\delta W_\delta$), that is if E be an element of K_δ.

7. Summarizing we observe:

If the productaggregate VW has been covered with numbers and if the aggregates G of those numbers corresponding to a same element of V converge uniformly to their limits L_G (as regards the covering of the positive numbers by the parts of W), the aggregates H of the numbers corresponding to a same element of W having the limits L_H (as regards the covering by the parts of V), then the aggregate of the numbers L_G (as regards the covering by the parts of V) has a limit, which is at the same time the limit of the numbers L_H (as regards the covering by the parts of W) and is the limit of the whole aggregate of numbers (as regards the covering by the parts of VW).

The equality of the two first-mentioned limits means *commutativity of two limittransitions.* One of the limittransitions relates to the covering by the parts of W, the other to the covering by the parts of V.

Chemistry. — *"On the Condensation of Formaldehyde with some Unsaturated Compounds."* By H. J. PRINS. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of May 3, 1919).

Some time ago [1]) the author discussed the mutual condensation of unsaturated compounds, examining the condensation of formaldehyde with styrol, anethol, isosafrol, pinene, d. limonene, camphene and cedrene. The condensation was effected either by warming the components in acetic acid solution, or by sulphuric acid in an aqueous or acetic acid solution. For the aqueous solutions we availed ourselves of the 40% solution as supplied by the trade, the acetic acid solution was obtained by warming trioxymethylene in acetic acid with or without the presence of sulphuric acid.

The aqueous and acetic acid solutions of sulphuric acid and formaldehyde behave differently as regards certain compounds, styrol, camphene and cedrene react but extremely slowly or not at all with the aqueous solution whereas anethol and isasofrol do react.

Contrary to isosafrol safrol does not affect an aqueous solution.

It many be assumed, that the reaction begins with an addition of the CO group to the C = C group, so that primarily a four-ring is formed.

$$R.H.C=C.H.R + H_2CO = R.H.C(-H_2C-O)-C.H.R$$

The four-ring can now:

1. absorb water and form a 1.3 glycol: $R.H.C(-H_2COH)-CHOH.R$

2. absorb formaldehyde and form a methylene ether:

$$R.HC(-H_2C-O-CH_2)-CH.R$$

[1]) Chem. Weekbl. **10**, 1003. (1913).
ibid. **14**, 932. (1917).

3. either directly by isomerisation, or indirectly via the glycol, pass into an unsaturated primary alcohol:

$$R . \underset{\displaystyle CH_2 OH}{\underset{|}{C}} = CH . R$$

If acetic acid is also present, acetates may be formed either of the glycol, or of the unsaturated primary alcohol.

In an aqueous solution we find with anethol and isosafrol a pretty exclusive and almost quantitative formation of the methylene ether.

In an acetic solution in the presence of sulphuric acid both a diacetate and a methylene ether are formed, cedrene and camphene yield in these circumstances an acetate of an unsaturated, primary alcohol.

Camphene, d. limonene and pinene yield in an acetic solution at the boiling-point of acetic acid likewise an acetate of an unsaturated alcohol besides other compounds with a higher boiling-point.

The mutual reaction of formaldehyde, pinene and limonene causing the formation of an unsaturated primary alcohol has already been observed by KRIEWITZ [1]), who brought about a reaction of the components by heating them in the presence of alcohol at a high temperature.

Prior to this, the formation of a primary, unsaturated alcohol has been ascertained by LADENBURG in the reaction between formaldehyde and a tetrahydropyridine-derivate.

Except with the terpenes the condensation affords good results, ranging from 70°/₀ to 90°/₀, of those theoretically possible; with the terpenes various products come into existence probably because the resulting unsaturated alcohol once more absorbs formaldehyde. The terpenes, containing more than one C = C group, there is besides a prior possibility of absorbing more than one molecule of formaldehyde.

The author likewise observed the setting in of suchlike reactions with amylene, citronellol, methylheptenon, citronellal, undecylenic acid, aethyl-cinnamate.

Experimental part.

Styrol and formaldehyde.

To a mixture of 33 gr. trioxymethylene and 320 gr. glacial acetic acid 32 gr. strong sulphuric acid was added, the trioxymethylene being solved by means of heating, then it was cooled down to 40° and while the mixture was shaken and occasionally refrigerated 104 gr. styrol was added in small quantities. If the temperature is allowed to rise beyond 50°, polymerization of the styrol sets in. The

---

[1]) Ber. d. deutsch. chem. Ges. **31**, 57. (1899).
ibid, **32**, 288, 2699 (1898).

mixture is allowed to remain overnight, then it is poured into water, taken up in ether and washed with a soda-solution. After drying and evaporating the ether, the diacetate amount can be determined by saponification. This proved to be 40 %. Then the oil is saponified with rather more than the theoretical quantity of alcoholic potassium and distilled in vacuum. By fractionation we can separate into:

Methylene-ether of 2.phenylpropylglycol. 1.3.

Colourless oil, boiling-point 128°—130°, pressure 13 mm. $D.\frac{18^0}{4^0} = 1{,}1111$. $N_d^{18^0} = 1{,}53063$.

Mol. refr. 45.64 (formula of LORENZ—LORENTZ). Calculated 45.87 (atom refr. according to EISENLOHR [1]).

The molecular weight determination in benzene gave: 162 and 156. Calculated for $C_{10}H_{12}O_2$: 164.

Analysis: % C determ. 71.6 and 71.1 Calc. for $C_{10}H_{12}O_2$ 73.2.
% H determ. 8.3 and 7.9 Calc. 7.3.

2. Phenylpropylglycol. 1.3.

Colourless, viscous liquid, boiling-point 176° pressure, 13 mm. $D\frac{19^0}{4^0} = 1.1161$. $N_d^{19^0} = 1.54267$. Mol. refr. 42.92. Calc. 43.21.

It yields quantitatively a diacetate boiling-point 162°—164° pressure 13 mm. (chemically bound acetic acid determined by saponification with alcoholic potassium). Molec. weight of the glycol. in benzene 257 and 189. Calcul. 152. Hence it is very strongly associated in this solvent; in a weak solution a normal molecular weight is obtained [2])

Analysis: found % C 70,6 and 70,9, Calc. C_9 H_{12} O_2 71,0.
% H 9,2 and 8,9, Calc. 7,9.

Both methylene ether and glycol are saturated as regards a solution of bromine in CCl_4, but while the methylene ether does not react with a solution of ethylmagnesiumbromide in ether at a normal temperature, the glycol immediately reacts. If toluol is added, raising the temperature to 100°, the methylene ether reacts exceedingly violently with the GRIGNARD solution. The fact that the glycol yields a diacetate when boiled with acetic acidanhydride and sodiumacetate is a proof of its two primary alcoholgroups, the isomeric-glycol, which might arise from the reaction between formaldehyde and the C = C-group of the styrol, would be a secondary-primary glycol with the phenylgroup attached to the secondary carbon atom and in the above-mentioned circumstances it would certainly lose water

[1]) Zeitschr. f. phys. Chem. **75**, 585. (1910).

[2]) Chem. Weekblad **16**, 929. (1919).

and yield the acetate of cinnamic alcohol. The latter could not be found.

Anethol and formaldehyde.

One grammol. anethol is stirred with a solution of two grammol. formaldehyde in 30 % sulphuric acid for three days, the product separated in the usual way yields, when distilled in vacuum:

Methylene ether of p. methoxyphenylbutylglycol.

A colourless, viscous liquid, boiling-point 168°—170° pressure 13 mm. $D\frac{16^0}{4^0} = 1.1197$, $N_d^{16^0} = 1.53438$. Mol. refr. 57.78 Cal. 56,74.

It does not react with a GRIGNARD-solution at a normal temperature and does not decolorize a bromine-solution.

Various efforts made to saponify the methylene ether to the correspondent glycol failed, resinification always set in or the ether remained unaltered. By leaving the ether for a fortnight in contact with 85 % formic acid, an oil was obtained, in which such an amount of formic acid was chemically bound as corresponded to 35 % di-formiate; saponification and distillation however, yielded an inconstantly boiling liquid.

Oxydation of the methylene ether.

In order to demonstrate, that with the anethol the formaldehyde had really reacted with the C=C group from the side-chain, the methylene ether was oxydized with potassium-permanganate. An acid was obtained with a meltingpoint of 182°—183°, and which revealed no depression when mixed with anisic acid.

Hence it appears, that in these circumstances formaldehyde does not react with the benzene nucleus.

Analysis of the methylene ether:

Found % C 70,1, 68,2 and 69,2. Calc. for $C_{12}H_{16}O_8$ 69,2.
% H 7,4, 7,8 Calc. 7,7.

Mol. weight in benzene: found 203 and 208. Calc. as $C_{12}H_{16}O_8$: 208.

Isosafrol and formaldehyde.

The condensation is effected in the same way as with the anethol. It gives:

Methylene ether of 3,4 dioxymethylenephenylbutylglycol.

Colourless, viscous liquid, boiling-point 182°—184° pressure 13 mm. $D\frac{17^0}{4^0} = 1,2272$. $N_d^{17^0} = 1,54078$.

Mol.refr. 56,84. Calc. 56,18.

Mol.weight in benzene: found 220 and 213. Calc. for $C_{12}H_{14}O_4$: 222.

Analysis:

Found % C 64,5 and 64,8. Calc. as $C_{12}H_{14}O_4$ 64,8.
% H 6,9 and 7,7: Calc. 6,3.

Camphene and formaldehyde.

A mixture of 30 gr. trioxymethylene, 130 gr. camphene and 136 gr. glacial acetic acid is boiled for three days, the oil separated by means of water, is dried, whereupon it is converted into an acetate by boiling it with an equal weight of acetic anhydride, which is called homo-camphenol acetate owing to its being derived from a homo-camphene:

Homo-camphenolacetate:

Colourless oil, boiling-point 124°—128° pressure, 13 mm. $D\frac{19^0}{4^0} = 1{,}0013$ $N\,{}^{19^0}_{d} = 1{,}48209$.

Mol.refr. 59.23. Calc. for a substance $C_{13}H_{20}O_2$ with one C = C group: 59.02.

Homo-pinenol.

By boiling pinene with tryoxymethylene and acetic acid in the way as indicated for camphene, an oil is obtained containing much chemically bound acetic acid, yielding after saponification and fractionation:

Colourless oil, boiling-point 113°—116° in vacuo, pressure 13 mm. $D\frac{19^0}{4^0} = 0.9720$. $N^{19^0}_{d} = 1.48616$.

Mol.refr. 49,05. Calc. for $C_{11}H_{18}O$ with one C = C group 49,66, for $C_{11}H_{18}O$ with two C = C groups: 51,39.

Mol. weight in benzene: found 188 and 190. Calc. 166.

Homo-limonenol.

Limonene is brought into reaction with formaldehyde in the manner as described for camphene, and the alcohol is separated as indicated for the pinene.

Colourless liquid boiling-point 122° — 126° in vacuo, pressure 13 mm. $D\frac{19^0}{4^0} = 0{,}9757$, $N^{19^0}_{d} = 1.50261$.

Mol. refr. 50,26. Calc. for $C_{11}H_{18}O$ with two C=C-groups 51, 39.

Analysis.

Found % C 78,1 and 77,7. Calc. for $C_{11}H_{18}O$ % C 79,5.
% H 11.6 and 11,7. Calc. % H 10,9.

These results agree with those of Kriewitz, l.c.

Cedrene and formaldehyde.

A mixture of cedrene with the equivalent quantity of formaldehyde in a 15 % solution of sulphuric acid in acetic acid, is stirred for three days. The reaction product is saponified and distilled in vacuum.

Besides other products with a considerably higher boiling-point there is obtained: Homo-cedrenol.

Colourless viscous liquid boiling-point 168°—171° in vacuo, pressure 13 mm. $D_{4^0}^{19^0} = 1{,}0270$. $N_d^{19} = 1{,}51826$.

Mol. refr. 69,08. Calc. for $C_{16}H_{26}O$ with one C = C-group 70,55.

As an alcohol it immediately reacts with GRIGNARD-solution and with acetylchloride, it discolorizes a bromine-solution.

Analysis.

Found °/₀ C 81,6 and 80,7. Calc. for $C_{16}H_{26}O$ °/₀ C 82,0.
°/₀ H 12,0 and 11,3. °/₀ H 11,1.

The principal aim of this investigation was: to demonstrate that formaldehyde reacts with a C = C-group in the way as indicated in the author's general scheme for the reactions between unsaturated compounds.

Hilversum, April 1919.

Botany. — "*Photo-growth reaction and disposition to light in Avena sativa*". By H. L. VAN DE SANDE BAKHUIJZEN. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of May 3, 1919.)

Of late years our knowledge of the influence of light on the longitudinal growth of plants has been considerably extended and deepened. While earlier investigations were generally content not to make their first observations until some hours after the beginning of illumination, attempts were made in more recent investigations to study as closely as possible from the very beginning of exposure the changes to which growth is subjected.

In 1914 BLAAUW published his investigations on the photo-growth reaction in *Phycomyces* [1]), and VOGT found in 1915 a similar reaction in the coleoptiles of *Avena* [2]); besides two further papers were published by BLAAUW on this reaction in seedlings of *Helianthus* [3]) and in certain roots [4]).

All these investigations were carried out under the influence of the new points of view which BLAAUW and FRÖSCHEL had opened up in 1909 on the subject of phototropy; hence attention was not confined to the intensity, but a definite amount of light energy was administered. In some cases illumination was continuous throughout the experiment.

While VOGT does not discuss the theoretical bearing of his results, BLAAUW uses his photo-growth reaction as a basis for a discussion of the phenomena observed in phototropy. Formerly it was indeed known that phototropic curvatures arise through growth being changed somehow by unilateral illumination, but since it was not known that a brief omnilateral illumination has an effect on longitudinal growth, it was impossible to obtain any accurate conception of the changes which growth underwent immediately on unilateral

---

1) A. H. BLAAUW. Licht und Wachstum. I. Zeitsch. f. Botanik. 1914.

2) E. VOGT. Uber den Einflusz des Lichts auf das Wachstum der Koleoptile von Avena sativa. Zeitschrift f. Botanik. 1915.

3) A. H. BLAAUW. Licht und Wachstum. II. Zeitschr. f. Botanik. 1915.

4) A. H. BLAAUW. Licht und Wachstum. III. Mededeelingen van de Landbouwhoogeschool. Deel XV. 1918.

illumination. This was one of the reasons why phototropy was regarded as a thing apart.

Blaauw once more defends the old theory of De Candolle and regards unilateral as a special case of omnilateral illumination; the former would thus have no specific action. If omnilateral illumination gives a photogrowth reaction uniform in all directions, unilateral illumination will only differ in giving an unequal growth reaction on the posterior and anterior sides. Here it is not the difference of light, but the light itself, as energy, which influences the longitudinal growth of every cell, but since the front is differently lighted from the back, the two sides will show unequal changes in growth. The result of this inequality is a curvature towards the source of light or away from it; this is the phototropic curvature. By these considerations phototropy has been saved from its isolation and has become susceptible of deeper and more exact analysis. A further important point is, that Blaauw ascribes an influence to the posterior side also, which quite corresponds to that of the anterior. It is not the anterior nor the posterior side alone which actively causes the curvature; both are concerned: it is the difference in the change of growth of the two sides which makes the plant curve phototropically.

The possibility that unilateral illumination might be a special case of omnilateral, i. e. that every longitudinal strip of the plant might receive a photo-growth induction independently of the rest of the circumference and might execute a photo-growth reaction, suggested an investigation of the question, whether this could throw any light on various phototropic phenomena described in the literature. I found that the photo-growth reaction gives us the means of explaining satisfactorily many apparently contradictory phenomena. Since phototropism has been most fully examined in *Avena sativa* and since Vogt moreover found a photo-growth reaction here, I have made a study of the literature on this plant. While I was engaged in working up these considerations for a preliminary publication, a paper by Bremekamp [1]) appeared, which gave me no reason to change my opinion; I hope to return to this more fully in a later paper.

Vogt illuminated coleoptiles of Avena from above with various intensities during periods of various length, but on this account his energy numbers are not comparable with horizontal light. By the first method the plants receive much less light, since the absorbent surface is much smaller. With horizontal illumination we need apply

---

[1]) C. E. B. Bremekamp. Eine Theorie des Phototropismus. Recueil des Travaux bot. néerlandais. Vol. XV. 1918.

much less light energy in order to obtain the same reaction, than with light coming vertically from above. Therefore the intensity and the energy numbers must be divided by a certain coefficient.

Now VOGT found that already after a few minutes the rate of growth began to fall off. This led after about 25 minutes to a minimum, while after 30—40 minutes the zero point was again passed. Then an acceleration of growth occurred, leading to a maximum, so that at about 60 minutes after the beginning of illumination the first rate of growth had been reestablished. After that the growth oscillated for a long time, at first with considerable but later with gradually decreasing maxima and minima.

I have now calculated from VOGT's tables [1]), how many μ the plants grew less during the first retardation period than if they had continued their growth in the dark. The following figures therefore give, in μ, the total retardation of growth until the zero-point is again reached and the acceleration of growth begins. It should always be remembered that the intensity numbers must be divided by a coefficient before being comparable to those of horizontally incident light.

TABLE I.

Intensity.	Duration of illumination.			
	1 min.	3 min.	15 min.	continuous.
16 M.C.		39		83
64 M.C.	53			
100 M.C.	102	104	90?	
500 M.C.			122	123
1000 M.C.		294	76	147
1500 M.C.			89	

Since in unilateral illumination the front is always more strongly illuminated than the back, the former is retarded more than the latter, if the retardation of growth increases with increasing intensity. Consequently a positive phototropic reaction occurs, provided the difference in growth retardation is sufficient to give a visible curvature. If the retardation of growth diminishes again with increasing intensity, a negative reaction will occur, for in this case the back side is retarded more than the front. It is seen from the table that the first and second columns will give positive curvatures. We cannot

[1]) VOGT l.c. Tables 8, 9 and 11.

conclude from the third column whether the numbers increase or decrease, they are not sufficiently certain. If we, however, arrange the first and the second column according to quantities of energy the figures rise, hence, we might expect much higher figures in the third column. Probably we are here beyond the maximum of growth retardation. On the other hand the figures rise again on prolonged continued illumination; this completely agrees with the fact, that illuminations of longer than 25 mins. always give positive curvatures. Now since it is known that phototropic curvature can already be detected after 25 mins. by means of a microscope [1]), a sufficient difference in growth between the two sides must have occurred in this time. If the photo-growth reaction is therefore to be regarded as the basis of phototropic curvature, the numbers, giving the retardation of growth to 30 minutes after the beginning of exposure, must provide a clue [2]). The occurrence of curvatures at the extreme apex within 25—30 mins. can therefore be sufficiently explained by growth retardation alone. There are however further points, which indicate that the acceleration of growth, following the retardation, has nothing to do with the establishment of the curvature.

When the acceleration of growth is over, the growth curve still shows pronounced rises and falls. These are, however, not to be considered as oscillations about a condition of equilibrium, like those of a pendulum coming to rest, but must certainly be regarded as the reactions of zones situated below. Just as in a phototropic curvature the reaction first becomes visible at the extreme apex, the first period of retardation of growth must also represent the reaction of the extreme apex; the photo-growth reaction of the inferior zones will not occur until later. This is therefore quite comparable to the progress of the phototropic curvature from the apex to the regions further below. The magnitude of the later retardations of growth cannot however be deduced from the tables, since the average rate of growth does not remain constant, which is partly attributable to the great period, which itself is moreover influenced by light. [3])

---

[1]) E. Pringsheim. Studien zur heliotropischen Stimmung und Präsentationszeit. Zweite Mitteilung. Cohn's Beiträge zur Biologie der Pflanzen. Bd. IX. 1909.

W. H. Arisz. Onderzoekingen over Fototropie, Diss. Utrecht. 1914; Rec. trav. bot. Néerlandais. Vol. XII. 1915.

[2]) I neglect here the negative curvatures, which after a time may succeed to positive ones; these can be explained in a quite different manner, as I shall show in my detailed paper.

[3]) H. Sierp. Ein Beitrag zur Kenntnis des Einflusses des Lichts auf das Wachstum der Koleoptile von Avena sativa. Zeitschr. f. Botanik. 1918.

We are here concerned with a conduction of the photo-growth reaction; the magnitude of the growth retardation in the lower zones will likewise depend on the energy applied.

The curve, which represents the dependence of the growth retardation (ordinate) in respect of the energy applied in 5 mins. (abscissa), we call: *growth retardation curve*. From the numbers of table I we cannot very well construct this curve, as there are too few data. There is however every reason for assuming that there is an ascending portion which can bring about positive curvatures and a descending one producing negative ones. Hence somewhere there is a maximum; its existence and position will be determined later by another method. Since the rule of products will apply also to the photo growth reaction within certain limits, there belongs to every amount of energy (x) a definite retardation of growth (y) after a certain time (here $1^1/_2$ hour).

Now in unilateral illumination the front receives the full energy [1]); the back receives much less. If we are on the ascending part of the curve, the retardation of growth on the anterior side (y_a) is greater than that on the posterior side (y_p) and only a positive curvature will occur. Now 20 M.C.S. is the practical threshold value for a readily visible curvature; on applying this amount of energy therefore, there will occur a difference of growth retardation between the front and back, which is just sufficient to produce a curvature which can be readily detected macroscopically. The threshold value of 20 M.C.S. is however only applicable to plants which have been grown in the dark, and have received a quantity of light energy $= 0$. It is different with plants which have had an omnilateral fore-illumination. This can be done by rotating the plants before the source of light, so that successively all sides are illuminated; in this way all parts of the circumference receive an equal amount of light. If subsequently there is a unilateral illumination, the threshold value for a positive curvature is found to be much higher. I will now consider some experiments of Arisz [2]) on the socalled "disposition (German "Stimmung") to light" in oats and in the first place the omnilateral fore-illumination with less than 2000 M.C.S. applied within 3 minutes with an intensity below 25 M.C. The unilateral after-illumination always took place immediately after the omnilateral.

I find that all the changes, produced by the omnilateral

[1]) Reflection etc. is here left out of account.

[2]) Arisz l.c. Tables 24 and 25. See also Arisz: Adjustment to light in oats. Proceedings Kon. Ak. v. Wet. Amsterdam. 1913.

fore-illumination, can be satisfactorily explained by assuming that at every point of the circumference the energy of the unilateral after-illumination is simply added to that of the fore-illumination. The retardation at a given point of the circumference will therefore depend on the total energy received from the two illuminations together. If the energy difference between the anterior and posterior sides is then sufficiently great to give the difference of growth retardation required for a visible curvature, the threshold value will be reached. I have nowhere assumed a change in sensitiveness, in contradistinction to BREMEKAMP [1]), who attempts to explain the increase in the threshold value by the hypothesis, that the plant has become less sensitive as a result of the unilateral fore-illumination and thus imagines a change in the perception-basis.

If we apply unilaterally b M. C. S., the front will receive b, and of this the back $\frac{b}{m}$ M. C. S.; m is greater than 1, since the back receives less than the front. If we had, however, previously given a M. C. S. omnilaterally, the later front would have received of this $\frac{a}{n}$ M. C. S., the later back also $\frac{a}{n}$ M. C. S.; a unilateral after-illumination will then supply to the front in addition b M. C. S., altogether therefore $\frac{a}{n} + b$ M. C. S.; the back receives altogether $\frac{a}{n} + \frac{b}{m}$ M. C. S. In both cases the absolute energy difference between the front and back remains constant, i. e. $b - \frac{b}{m} = b\frac{m-1}{m}$ M. C. S. Now the resultant curvature entirely depends on the difference of growth retardation, which corresponds to an energy difference of $b\frac{m-1}{m}$ M.C.S. If the growth retardation curve were a straight line, there would always correspond to an energy difference of $b\frac{m-1}{m}$ M.C.S. one and the same difference of growth retardation, whatever place of the abscissa we may consider; the threshold value would then necessarily be constant. If the growth retardation curve is, however, a curve with decreasing slope, the growth retardation difference corresponding to an abscissa difference of $b\frac{m-1}{m}$ M. C. S. will become the smaller, the gentler

[1]) BREMEKAMP l.c.

the slope of the curve becomes, i.e. the greater x becomes.

We call the energy on the anterior and posterior sides respectively x_a and x_p, the retardations of growth y_p and y_a.

growth retardation

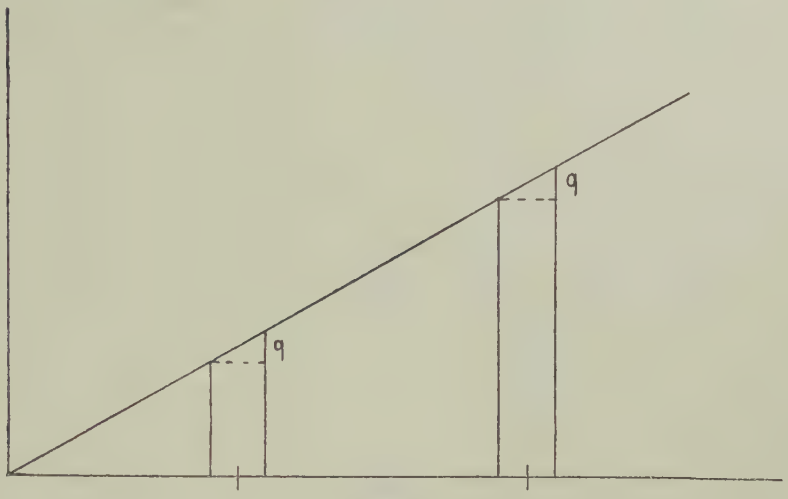


Fig. 1. energy

In a straight with $x_a - x_p$ constant $= b\,\frac{m-1}{m}$ M.C.S. the difference in growth retardation $y_a - y_p$ is always $= q$ (fig. 1).

In a curve with decreasing slope, with $x_a - x_p$ constant $= b\,\frac{m-1}{m}$ M. C. S. the difference in growth retardation $y_a - y_p$ is smaller, according as x_a is larger (fig. 2).

Now x_a will become greater by omnilateral fore-illumination, for $x_a = \frac{a}{n} + b$ M.C.S. The absolute energy difference $b\,\frac{m-1}{m}$ M.C.S. or rather the energy of b M.C.S. applied unilaterally, will therefore give a smaller difference of growth retardation i. e. a smaller curvature, according as the energy of fore-illumination a is greater. In order nevertheless to obtain a constant difference of growth retardation, giving a just visible curvature, $b\,\frac{m-1}{m}$ and therefore also b will have to be greater.

If the energy of fore-illumination becomes greater, the threshold value will rise, as soon as the curve of growth retardation is a curve with decreasing slope. Here we need not yet assert anything about the further relation between the magnitude of the slope and x.

In our case we can however follow the course of the growth retardation curve more closely by attempting to trace the relationship between threshold value and fore-illumination. If we calculate

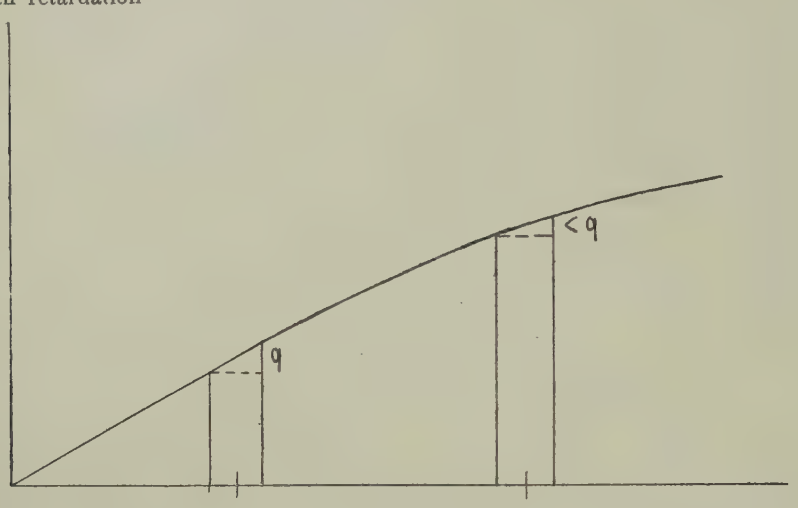


Fig. 2.

from ARISZ's tables, mentioned above, the ratio of unilateral after-illumination to omnilateral fore-illumination, we find that, if after-illumination : fore-illumination $= 1 : 11$, there is no curvature;

with this ratio 1 : 10, 9.9 or 9.2 a few plants give a feeble positive curvature,

with the ratio 1 : 7.2 all plants curve positively.

This applies, as was already said above, only to a fore-illumination of less than 2000 M.C.S. given within 3 min. with an intensity below 25 M.C. We must, however, recalculate this for the quantities, which the anterior and posterior sides receive. Since we see, that a feeble positive curvature occurs when the ratio after-illumination : fore-illumination $(b : a)$ has reached a definite magnitude 1 : 9.7, the ratio of the energy difference $b\frac{m-1}{m}$ to the energy of the anterior side $\frac{a}{n} + b$ must also be constant, whatever be the values of m and n. In order to demonstrate this numerically, I propose to make certain assumptions respecting m and n; in principle it does not matter, what values we ascribe to m and n. For m I assume 4; the back is then illuminated with $^1/_4$ of the intensity of the front, receives therefore in unilateral after-illumination $\frac{b}{4}$ M.C.S. Since the omnilateral energy a M.C.S. is distributed uniformly over the whole

circumference, each half, viz. the later anterior or posterior sides, will receive, to begin with, half of the energy, $^1/_2\ a$ M.C.S. Moreover each point, which is turned away from the source of light, receives during rotation a further $^1/_4$ of the energy of the illuminated side; each half receives therefore altogether $\frac{5}{4} \times \frac{1}{2}a = \frac{5}{8}a$ M.C.S.

Here follows a table, taken from tables 24 and 25 of Arisz; I have added the numbers representing

$$100 \times \frac{\text{energy difference between front and back}}{\text{energy of front}} \left(= 100 \times \frac{x_a - x_p}{x_a}\right).$$

TABLE II.

Energy of omnilateral fore-illumination in M.C.S.	Energy of the unilateral after-illumination in M.C.S.					
	$\frac{4\times5.5}{22}$	$\frac{8\times5.5}{44}$	$\frac{5\times12}{60}$	$\frac{10\times12}{120}$	$\frac{5\times100}{500}$	$\frac{10\times100}{1000}$
0 = 0	75 +	75 ++	75 ++	75 ++	75 ++	75 ++
10 × 5.5 = 55	29.5 +	42.3 ++	47.9 ++	58.4 ++	70.2 ++	72.5 ++
10 × 12.1 = 121	17 +	27.7 +	33.3 ++	46.2 ++	65.2 ++	69.8 ++
36 × 12.1 = 435	5.6 0	10.4 +?	13.6 +	23 +	48.6 ++	58.9 ++
100 × 5.5 = 550	4.5 0	8.5 0	11.1 +?	19.4 +	44.4 ++	55.8 ++
100 × 12.1 = 1210	2.1 0	4.1 0	5.1 0	10.3 +?	30 ++	42.7 ++

Explanation: ++ all plants show strong positive curvature.
+ all plants show definite positive curvature.
+? a few plants show slight positive curvature.
0 no plants curved.
10 × 5.5 means: during 10 sec. omnilateral fore-illumination with 5.5 M.C.

$$29.5 = 100 \times \frac{b\frac{m-1}{m}}{\frac{a}{n} + b} = 100 \times \frac{\frac{3}{4} \times 22}{\frac{5}{8} \times 55 + 22}.$$

I here assume +? as the threshold value. We see that for this the quotient $100 \times \frac{x_a - x_p}{x_a} = 10.4$, 11.1 and 10.3, and it is therefore sufficiently constant. Then $y_a - y_p$ has become so great that a slight positive curvature occurs. If the curvature can be represented by $f(x_a) - f(x_p)$ and also by $\varphi\left(\frac{x_a - x_p}{x_a}\right)$ then f is necessarily $c \log x$ as can be readily shown by a simple mathematical consideration. Since the region of energy, about which the figures supply information, extends from about 300—900 M.C.S. we may say that this portion of the growth retardation curve has a logarithmic course. If the

quotient $\frac{x_a - x_p}{x_a}$ for the threshold value had not been found constant, we should only have been allowed to conclude, that the growth retardation curve was a curve with decreasing slope, since the threshold value increases with increasing x. In that case also we might perhaps have obtained some further information about the function. I emphasize here that no fundamental significance should be attached to the logarithmic course of this part of the curve between 300 and 900 M.C.S. Moreover the curve from 0—100 M.C.S. is certainly not logarithmic; in a subsequent paper I hope to refer to this point in detail.

Arisz regards the omnilateral fore-illumination followed by a unilateral after-illumination as a combination of unilateral illuminations, a short one on the posterior side (fore-illumination) and a longer one on the anterior side (fore-illumination + after-illumination). Since the later posterior side has also received energy during the fore-illumination, a tendency to curve in the opposite direction would have to be overcome. "It need cause no surprise, that the excess which must be given on one of the sides, to obtain an ipsilateral curvature, must be greater in proportion as the tendency to curvature on the other side is stronger." Arisz therefore likewise explains the rise in the threshold value without assuming a change in the sensitiveness. This "tendency to curve in the opposite direction" however, as has been explained above, also exists in plants which have had a purely unilateral illumination, for the curvature depends on the difference of growth retardation between front and back. As in a combined omnilateral fore-illumination and unilateral after-illumination the growth retardation on the posterior side i.e. the "tendency to curve in the opposite direction", becomes relatively greater, the difference in growth retardation and accordingly, also the resulting curvature, becomes smaller (Fig. II). Arisz regards the phototropic induction, and hence also the tendency to curve, as a primary reaction, but since according to the theory of Blaauw, which I have here worked out further, the growth retardation is primary and the tendency to curve secondary, it is better not to employ the latter expression, but to speak of a greater or smaller growth retardation. The unilateral illumination is a special case of the omnilateral and not inversely.

We see therefore, that it is of great importance to ascertain the course of the growth retardation curve. We could not well do this from the figures of table I; moreover the energy numbers had to be divided by a coefficient in order to make them comparable with those for horizontally incident light. We will now try to ascertain the position

of the maximum of the growth retardation curve in another manner.

A second phenomenon which shows itself in the combination of an omnilateral fore-illumination with a unilateral after-illumination, is that which CLARK [1]) calls the increase in sensitiveness of the negative reaction. Here also we can find a simple explanation if we suppose the existence of a descending portion in the growth retardation curve. If the front receives in unilateral illumination an amount of light energy just in excess of the maximum, then the back, which receives $\frac{1}{4}$ of this, will still be on the ascending portion. The ordinate of the front is still greater than that of the back, hence a positive curvature occurs. When we now apply more unilateral energy, we shall have to shift the points, representing the back and front energy, along the growth retardation curve, in such a manner that always $x_a = 4\,x_p$. A negative curvature will then only be possible much further on, because of the great distance between x_a and x_p, i.e. x_a will have to pass far beyond the maximum before y_a becomes smaller than y_p; x_p need not yet have passed beyond the maximum. When then the negative difference of growth retardation $y_a - y_p$ is great enough to become visible in a curvature, a negative curvature will occur (about 5000 M.C.S. if administered in 5 mins.). This becomes different, however, if x_a and x_p both lie on the descending portion and are less remote from each other; in that case, as soon as x_p has passed the maximum, the possibility of a negative curvature will arise, the front however requires to receive much less than $4x_p$ in order still to render a visible negative curvature possible. By means of an artifice we can arrange that x_a and x_p come near to each other, although both are on the descending portion. This artifice consists in giving an omnilateral fore-illumination with a quantity of light, which is so great, that front and back both receive a quantity of energy corresponding to the maximum of the growth retardation curve. If we then unilaterally apply an amount of energy, which by itself would have given a strongly positive curvature, there will occur a negative curvature, at least if $x_a - x_p$ is so large that $y_p - y_a$ can give a visible effect. Here also the magnitude of the difference of growth retardations, and hence the threshold value for the negative curvature, will depend on the slope of the growth retardation curve, as was the case with the positive curvature. Here some data from tables 25 and 26 of ARISZ are appended; I have added the numbers representing the quantities of light in M.C.S. which the front and back receive from omnilateral fore-illumination + unilateral after-illumination.

[1]) O. L. CLARK. Uber negativen Phototropismus bei Avena sativa. Zeitsch. f. Botanik. 1913.

TABLE III.

Energy of unilateral after-illumination in M C. S.	Omnilateral fore-illumination.					
	12.1 M. C. during 180 secs.			25 M. C. during 100 secs.		
	Energy to front in M. C. S.	Energy to back in M. C S.	Reaction.	Energy to front in M. C. S.	Energy to back in M. C. S.	Reaction.
44	1405	1372	0	1606	1573	0
60	1421	1376	0	1622	1577	0
120	1481	1391	?	1682	1592	0
500	1861	1486	?	2062	1687	?
1000				2562	1812	?

Explanation:

The energy to the front, 1405 M. C. S., is calculated from $\left(\frac{a}{n}+b\right)=\left(12.1\times180\times\frac{5}{8}+44\right)$ M. C. S., that to the back, 1372 M. C. S, from $\left(\frac{a}{n}+\frac{b}{m}\right)=\left(12.1\times180\times\frac{5}{8}+11\right)$ M. C. S.

Arisz means by the sign? that "some plants give a feeble positive curvature, but there are always a few which curve negatively"; this has been confirmed by clinostat experiments. He directly connects this phenomenon of "increased sensitiveness to the negative reaction" with the fact, that after 300—600 M.C.S. the strength of the maximal curvature diminishes, and considers it possible that "by combining a quantity of light, which gives a curvature in excess of the greatest maximal strength, with a quantity which is maximal or nearly so, a curvature is obtainable towards the weaker illumination". We may not connect the "decreased sensitiveness to the positive reaction" with the tendency to curve in the opposite direction and as little may we here directly connect the "increased sensitiveness to the negative reaction" with the strength of the maximal curvature, but must explain it from the course of the growth retardation curve. For the maximal curvature will be strongest in that case, where the difference between the ordinates belonging to x_a and $\frac{1}{4}x_a$ is a maximum. The decrease in the amount of this difference is primarily connected with the decrease in slope of the growth retardation curve and it is only the rate at which the curvature diminishes at higher amounts of energy or the change to a negative curvature, which is connected with the question whether or no the growth retardation curve presents a maximum. The growth retardation curve will therefore continue to rise, although the intensity of curvature (i.e. the difference between the ordinates belonging to x_a and $\frac{1}{4}x_a$) is already declining; the maximum will

therefore be situated much higher than 300—600 M. C. S. Now it results from the above table that if the back receives about 1400 M.C.S., negative curvatures may occur. In this neighbourhood therefore the maximum of the growth retardation curve must lie; there may be considerable individual variation; if the maximum lies somewhat higher, a feeble positive reaction will still be possible; if it is at or below 1400 M.C.S., negative curvatures can occur, this depends on the degree of slope of the descending portion. We can also calculate from table II that a negative curvature never occurs, if the back receives less than 1400 M.C.S. Thus 1756 M.C.S. on the front and 1006 M.C.S. on the back still give a strong positive curvature; here the y of 1756 M.C.S. must be greater than the y of 1006 M.C.S. We may therefore place the maximum of the growth retardation curve at about 1400 M.C.S.

With a unilateral illumination the posterior side will not be maximally retarded until the anterior receives $m \times 1400$ M.C.S. This amount of energy must of course lie beyond the threshold value for the negative curvature, for otherwise y_p could never become larger than y_a and no negative curvature could occur. From this the value of m can be found approximately.

I shall indicate yet a third method by which the course of the growth retardation curve can be explored. This can be done by assuming the magnitude of the maximal curvature to be proportional to the difference between the front and back growth retardation. If the maximal strengths of curvature are then plotted against the energy values as abscissae, there results a curve of the differences of growth retardation between the anterior and posterior sides. By a simple mathematical calculation, the growth retardation curve of the front can be calculated from the curve of differences, whereby it is assumed again, that the back receives $\frac{1}{4}$ of the energy of the front; here the magnitudes of the growth retardation do not of course represent absolute values. The points of the posterior growth retardations are found by subtracting the curve of differences from the anterior curve; these can also be found by plotting the anterior curve with abscissae four times as great (rule of products). The magnitudes of the maximal curvatures I have deduced from tables 1 and 3 of Arisz; the energy was here always applied in 10 secs. Since the front is exposed to the full energy [1]), we have here again plotted the course of the growth retardation curve. In this way we come to the following result:

---

[1]) See footnote p. 61.

from 0—75 M. C. S. the growth retardation curve is more or less rectilinear, then the slope decreases, so that it becomes approximately logarithmic from 300—700 M. C. S., while a maximum is found at about 1600 M.C.S. This value therefore agrees sufficiently well with that already found.

Finally I have also succeeded in finding theoretically the further course of the growth retardation curve, which explains both the phenomena attending more prolonged unilateral illumination and those of unilateral preceded by prolonged omnilateral illumination.

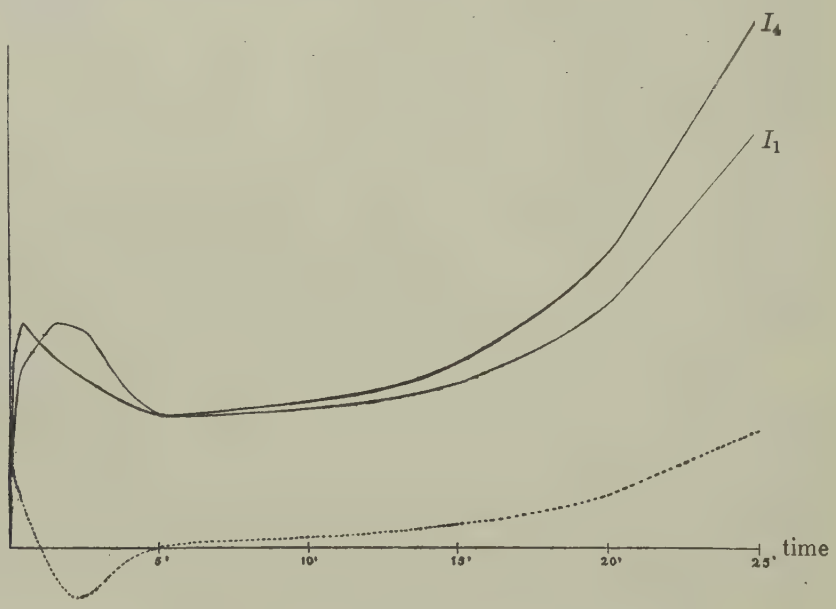


Fig. III. Diagrammatic representation of

——— the growth retardation curve for an intensity 1.
——— the growth retardation curve for an intensity 4.
..... magnitude of curvature occurring after unilateral illumination with intensity 4.

Here the growth retardation has not been represented as a function of the energy, but as a function of the time, during which there was illumination with the same intensity. Since unilateral illumination, following an omnilateral illumination of more than 5 minutes' duration, always results in a positive curvature, y_a must again be greater than y_p. This comes about through the renewed rise in the growth retardation curve, if the plant is illuminated for more than 5 minutes. Since the slope increases here, the threshold value for positive curvature must again fall. This latter fact agrees with what CLARK and ARISZ found, namely that the threshold value falls if the plants are submitted to a fore-illumination of more than 5 minutes and less

than 20 minutes. If the fore-illumination is more than 20 minutes, the growth retardation curve has become a straight line, since the threshold value now remains constant; however prolonged the fore-illumination with this intensity is, there is no further change in disposition. *Conversely there will be no question of "disposition", "change of sensitiveness", in a process where the effect increases in a rectilinear manner with increasing strength of stimulus.*

Now since also after unilateral continued illumination (for longer than about 5 mins.) a positive curvature is again obtained [1]), the growth retardation curve, for an intensity m times as great, will run more steeply, i.e. for the same abscissa (time) there will be a greater ordinate (retardation of growth). If we take, however, the growth retardations of different intensities with equal duration of illumination, and plot these against the intensities, the slope of the resulting curve will of course greatly decrease at higher intensities, as a simple consideration will show. With this two facts agree: firstly that the threshold value after prolonged fore-illumination with high intensities comes to lie higher than after prolonged fore-illumination with low intensities; secondly, that prolonged unilateral illumination with a high intensity gives a feebler curvature than illumination with a low intensity during the same period.

We see therefore that the phototropic curvature is determined by the reactions of the separate longitudinal strips of the front and back respectively. Formerly the curvature was regarded as the direct result of a single condition of stimulation, the phototropic, which was considered to be induced as such. According to the view set out above, the curvature must be regarded as the resultant of the effects arising from the conditions of stimulation, which exist on the side, towards which the ultimate curvature will take place, and on the opposite side. These conditions of stimulation express themselves in photo growth reactions; the difference between the two reactions is expressed by the phototropic curvature.

The cause of that which was formerly called "disposition" lies in the peculiarities of the growth retardation curve. These peculiarities occur to some extent in every process in which the reaction is not directly proportional to the stimulus. A tangent galvanometer also becomes less "sensitive" at greater strengths of current. The "disposition" at a given point of the growth retardation curve, whether we take energy or time as abscissa, depends therefore on the magnitude and the sign (+ or —) of the angle of slope, and of

---

[1]) See footnote 2 p. 60.

the direction in which the latter is changing. We can ascertain the sign by arranging that x_a and x_p approximate closely; then we can see from the curvature whether y_a—y_p is positive (effect: positive curvature) or whether it is negative (effect: negative curvature). In unilateral illumination x_a and x_p lie too far apart and may be on dissimilar parts of the curve, so that the latter is very difficult to draw. According as x_a and x_p approximate more closely, the angle of slope can be found with greater accuracy. Since we have found that the growth retardation curve shows an ascending, then a descending and subsequently again an ascending portion, the "disposition" must therefore have three phases; finally after 20 mins., it is not possible to bring about a "disposition change" by further illumination with this intensity. These three phases have been repeatedly discussed in the literature and explained as processes, involving a change in the perception basis. From the above discussion it is evident, however, that disposition is a concept devoid of specific properties and is simply an expression of peculiarities of the growth retardation curve. Every growth retardation curve has a maximum at about 1400 M.C.S. and a minimum at about 5 minutes. The growth retardation curves of two intensities, which are in the ratio 1: m and with which 5000 M.C.S. can be applied within 5 minutes, intersect at two points; the first point is the energy threshold for the negative curvature ($\pm$ 5000 M.C.S.), the second is the time threshold for the second positive curvature (5 minutes). It will, however, be easier and more accurate to construct the growth retardation curves, both energy curve and time curve, from the numbers for photo growth reactions than from interpolations according to the above mentioned method, which is only qualitative, but not absolutely quantitative. Phototropism retains its value, however, since the study of photogrowth reactions presents difficulties in so far as we are here certainly concerned with the conduction of stimuli, while we only observe the reaction of the whole plant. Since in phototropic curvature the various zones curve, one after the other, we get this conduction of stimuli here separated into its successive phases. The difference in growth retardation will also be more constant as phototropic curvature, than when it is found by examining the photogrowth reactions of two different plants, in one for a quantity of energy 1, in the other for a quantity of energy m. For in unilateral illumination both experiments are carried out on the same plant, one on the front, the other on the back. The difference, the resultant of the two reactions, will thus be less influenced by individual variability.

Utrecht, April 1919.

Astronomy. — *"The Structure of the Sun's Radiation"*. By P. H. VAN CITTERT. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of May 3, 1919).

It is known that the intensity of the light on the sun's disc very appreciably diminishes from the centre towards the limb, and that this takes place in a different degree for the different colours: regions near the limb[1]) of the sun's disc are distinctly ruddy as compared with the centre.

By the aid of a spectral photometer VOGEL[2]) determined this distribution of intensity for six regions of wavelength in the visible part of the spectrum. The decrease of intensity towards the limb appeared to be greater for light of shorter wavelength than for light of longer wavelength; the diminution, however, does not take place quite regularly with the wavelength, but presents an anomaly in the neighbourhood of 5000 $\mathring{A}$. the contrast of the limb to the centre is for this wavelength-region less than the contrasts for the other wavelength-regions would lead us to expect.

VOGEL's observations were repeated by ABBOT[3]) in 1906 by the aid of a bolometer. ABBOT determined the decrease of intensity for a great number of wavelength-regions in the infra-red and the visible spectrum. He also found a strongly pronounced wavelength-effect: the contrast towards the limb increased very greatly towards the violet. Also his observations presented an anomaly in the neighbourhood of 5000 $\mathring{A}$, though less pronounced than that in VOGEL's observations. In fig. 1 we have plotted as functions of the wavelength, what value the intensity has for places which are at a distance of 0.65, 0.825, and 0.95 of the radius of the sun's disc from the centre, when in the centre the intensity is put equal to 100 for all the colours. The data are borrowed from ABBOT's tables. It is seen that the intensity rapidly decreases towards the limb, and this the more rapidly as the wavelength is smaller, but at the same time the fact

---

[1]) In the present paper, the phenomena at the limb itself and even in regions, more than e.g. $\frac{95}{100}$ of the radius of the disc removed from the centre, are left out of consideration.

[2]) H. C. VOGEL, Berl. Ber., 1877.

[3]) C. G. ABBOT. Ann. of the Obs. of the Smiths. Inst., **2**, 205, 1908; **3**, 153, 1913.

strikes us that in the region 6000—4000 $\mathring{A}$ this decrease of intensity presents an oscillation. It is noteworthy that the maximum of energy of the sun's radiation lies at the same place in the spectrum.

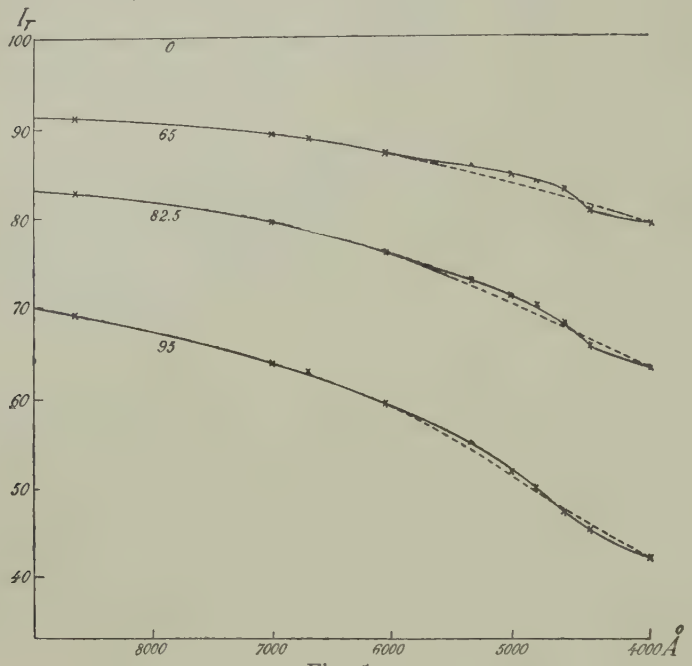


Fig. 1.

(Abbot's observations ranged from 21000 $\mathring{A}$ to 3800 $\mathring{A}$; the part from 21000—9000 $\mathring{A}$ has, however, been omitted in the figure, because the curves do not present an irregular course there, but gradually approach the line $I_r = 100$ towards 21000 $\mathring{A}$).

To account for this decrease of intensity towards the limb many investigators have considered the sun as a self-luminous uniformly radiating core, surrounded by a strongly absorbing atmosphere. Now the state in the sun's atmosphere must naturally be stationary on the average: the quantity of energy that the atmosphere absorbs, must be radiated again, even though it be in another form, and half must be radiated towards the outside. Now it has appeared convincingly from the observations of the annular eclipse of April 17th 1912 [1]) that of the total quantity of energy that the earth receives from the sun, at most one thousandth part can originate from the sun's atmosphere. It is, therefore, impossible that the absorption should be the chief cause of the diminution of intensity towards the limb.

[1]) W. H. Julius. These Proc. **15**, 1451.

Continuing the investigations of RAYLEIGH [1]), SCHUSTER [2]), KING [3]) and SCHWARZSCHILD [4]) on molecular scattering of light, SPIJKERBOER [5]) has treated the problem how the distribution of light on the sun's disc would be for the different colours, if exclusively molecular scattering in a non-absorbing and not self-luminous atmosphere were the cause through which the uniform radiation of a self-luminous solar core was modified. He arrived at a distribution of light which presents close resemblance to that observed by ABBOT.

The influence of the diffusion (or molecular scattering) is determined by the product $H = s.t$, in which $t =$ the thickness of the dispersive layer and $s = \frac{32\pi^3(n-1)^2}{3N\lambda^4} =$ RAYLEIGH's coefficient of scattering. When it is now assumed that t has the same value for light of different wavelengths, that the "core" lies, therefore, equally deep for all colours, the wavelength-effect is exclusively determined by the dependence of s on λ^4, because, when kinds of light in the neighbourhood of the proper-frequencies are left out of account, $(n-1)$ will vary very little along the spectrum. It appears, however, that the observed dependence of the wavelength is somewhat less great than theory would lead us to expect. This may be due to the fact that besides the *diffusion* another phenomenon appears, which has a similar influence on the distribution of light as diffusion, but which does not vary so much with the wavelength, e.g. scattering by *irregular refraction*, and possibly a very slight general *absorption*.

Now it is very probable that, particularly in the deeper layers of the sun's atmosphere, irregular refraction plays an appreciable part. The existence of a very irregular distribution of density in the solar gases can, indeed, not be doubted, the constant variations in the granulations and flocculi on the sun's disc point in any case to the existence of an intricate system of currents in that gas-mass, and these are not conceivable without differences of pressure and irregular density gradients accompanying them. The mean value of these gradients, which is small in the outmost layers of the sun, must at first increase as one gets deeper. At a certain depth the irregular density gradients must then on an average be of the same order of magnitude as e.g. the vertical gradient of our terrestrial atmosphere. A gas-mass of the dimensions of the solar atmosphere,

[1]) RAYLEIGH, Phil. Mag., (5). **47**, 375, 1899.

[2]) SCHUSTER, Astrophys. Journ., **21**, 1, 1905.

[3]) KING, Phil. Trans. R.S., A (212), 375, 1912.

[4]) SCHWARZSCHILD, Berl. Ber., **47**. 1183, 1914.

[5]) J. SPIJKERBOER, Verstrooiing van licht en intensiteitsverdeeling over de zonneschijf. Proefschrift. Utrecht 1917. Arch. Néerl., (3 A), **5**, 1, 1918.

quite honeycombed with irregular gradients of such average magnitude, would, as JULIUS[1]) has demonstrated, refract, deflect and disperse the rays of light that penetrate there, so strongly to all sides, that the gas would present itself to a distant spectator as a turbid medium; the volume parts in which the density can be considered as constant, and hence the light as rectilinear, would be too small to be observed separately at such a distance. Since the degree of refractional scattering is determined by $(n-1)$, and accordingly varies comparatively slowly with λ, the co-operation of this kind of scattering with the molecular scattering will weaken the mean wavelength effect, peculiar to the latter.

Besides, the diminution of the intensity from the centre towards the limb will be greater than would be the case if only diffusion were the cause of this diminution. Irregular refraction, therefore, lessens the difference between the rates of darkening towards the limb shown by the different wavelengths, but at the same time strengthens the average contrast between limb and centre.

As another possible cause of the fact that the observed wavelength-effect is slighter than the theoretical, SPIJKERBOER suggests that the light of the longer wavelengths, as it gets less greatly weakened by diffusion, might come to us from deeper layers of the sun than the light of shorter wavelength. This supposition, evidently, excludes the older hypothesis that the sun would have to be conceived as a well-defined core surrounded by a sharply defined atmosphere. The idea that the various radiations originate at different levels is more in agreement with the conception of the sun as a glowing gas-mass, of which the density and the temperature gradually diminish towards the outside. Since the light of greater wavelengths is much less weakened than that of shorter wavelengths, it will come to us from deeper layers of the sun. The infra-red light will, accordingly, be relatively more weakened by molecular scattering than would be the case if it only came to us from equally deep layers as the violet light.

From what depth the light comes to us is, however, not only determined by the diffusion, but also by the irregular refraction. As this is little dependent on the wavelength, the differences in depth for the different colours will not be so great as in the case that only diffusion played a part. If, as is very probable, irregular refraction plays the principal part, especially in the lower layers, the difference in depth must be comparatively slight.

---

[1]) W. H. JULIUS, These Proc. **16**, 264, 1913.

Let us now consider the question how, seen from this point of view, the radiation emitted by the sun in a direction w (fig. 2) must be composed. The outer layers of the sun will emit very little energy; proceeding towards lower layers the quantity of emitted energy increases, at first slowly, then more rapidly, in consequence of the increase of temperature and density. Let us suppose $d\,e\,f$ to be the layer outside which no appreciable quantity of energy is

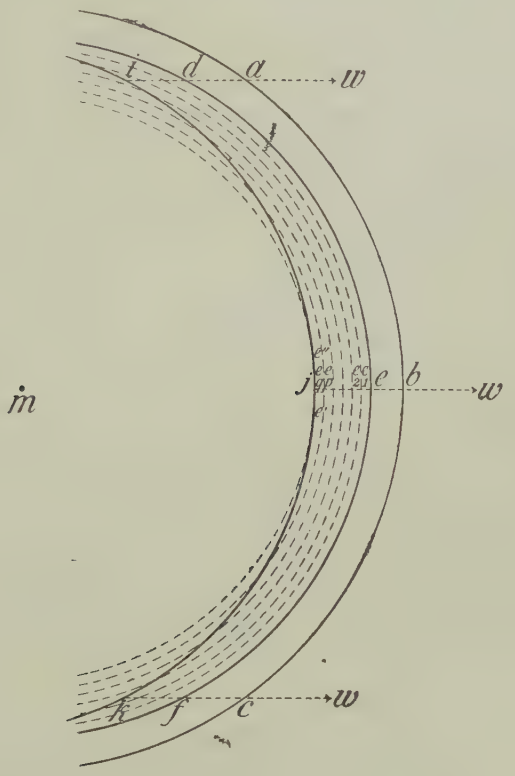


Fig. 2.

emitted. Let us first consider the radiation transmitted by the surface $d\,e\,f$ in the direction w. We shall take the scattering in the atmosphere outside $d\,e\,f$ later into account. From the region e_1 in the centre of the sun's disc w receives a comparatively slight quantity of radiation of comparatively low temperature, from e_2 a larger quantity of higher temperature, etc. At first the quantity of energy which w receives from the different depths, will increase; the deeper we get, however, the more will the emitted radiation be weakened by absorption, refractional scattering and diffusion. From e_p e.g. w will again receive less radiation than from e_2, but of higher temperature, from e_q very little, etc. Let us suppose that w does not receive an appreciable quantity of energy from layers lying deeper than j.

(It is noteworthy that w also receives radiation from e originating from regions e' and e'' in the neighbourhood of the radius vector je, which radiation has finally assumed the direction ew through diffusion and irregular refraction).

Let us now consider the energy curves of the radiations coming from those different regions, as functions of the wavelength. All of them will probably have the character of the curve of radiation of the absolutely black body: slow increase of the energy from the infra-red to a maximum, and then a comparatively rapid decrease on the violet side of the maximum. The loci of the maxima of the different curves are determined not only by the temperature of the corresponding radiations, but also by the relative importance of diffusion and refractional scattering. Since the light of shorter wavelengths is much more greatly weakened by diffusion than that of longer wavelength, the maximum will be displaced by the diffusion towards the side of the longer wavelengths; the irregular refraction, on the other hand, does not displace the maximum, because it is almost independent of the wavelength. For the curves belonging to the radiation originating from deeper layers, the maximum would lie more to the *violet* than for the curves belonging to the outer layers, if the *temperature* were the only factor; more to the *red*, however, if exclusively the *diffusion* were efficient. The height of the maximum is determined by the temperature of the radiation, the density at the places of emission, and the weakening which the radiation has undergone by diffusion, irregular refraction, and absorption.

We may therefore conclude that from the centre of the sun's disc a quantity of energy is emitted in the direction w of which the energy curve, proceeding from the infra-red towards smaller wavelengths increases, at first slowly, then more rapidly to a flat maximum, and then runs very steeply down to the violet (fig. 3 I).

Not far from the limb of the disc, e.g. at c (fig. 2), we shall receive light from a longer path through the gases ($ek > bj$), but it will come from less deep layers. Hence at the limb radiation is received from f only from the regions round kj lying more outwardly. The quantity of energy that w receives from the limb of the disc is therefore for all colours smaller than that which w receives from the centre. Hence the energy curve of the limb of the sun will as a whole lie lower than that of the centre. *If the diminution of energy were the same for all the colours*, the composition of the light at the limb would be represented by a curve which had the same shape as that of the centre (fig. 3 II). Now it is directly to be

seen that this cannot be the case, for the radiation at the limb will not present such a variety of temperature, irregular refraction,

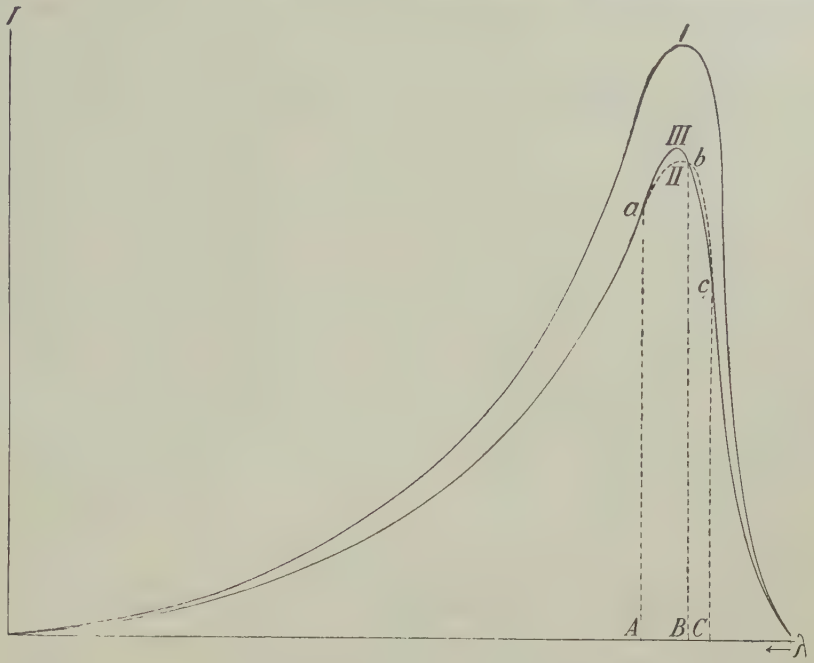


Fig. 3.

diffusion, etc. as that in the centre, because at the limb only radiation from a smaller number of layers contributes to the total radiation. The radiation at the limb will therefore have an energy curve with a maximum which is not so flat as that for the central radiation, and which, as we only receive radiation of lower temperature, lies somewhat more towards the side of the longer wavelengths (fig. 3 III).

When we now compare the curves fig. 3 I, II, and III, it appears that in the wavelength-region AB the limb radiation will have a relatively stronger, in BC a relatively slighter intensity than would be the case if the distribution of the energy were the same as in the centre.

When we now put the central radiation for all the wave-lengths $= 100$, this is graphically represented by a straight line C parallel to the wavelength-axis (fig. 4). The limb radiation can then be represented by an almost straight line r, which runs about parallel to the wave-length-axis, but which exhibits an oscillation in the region ABC.

These radiations will be weakened by the diffusion and irregular refraction in the atmosphere outside def (fig. 2), light of the shortest wavelengths most. When again we put the resulting central

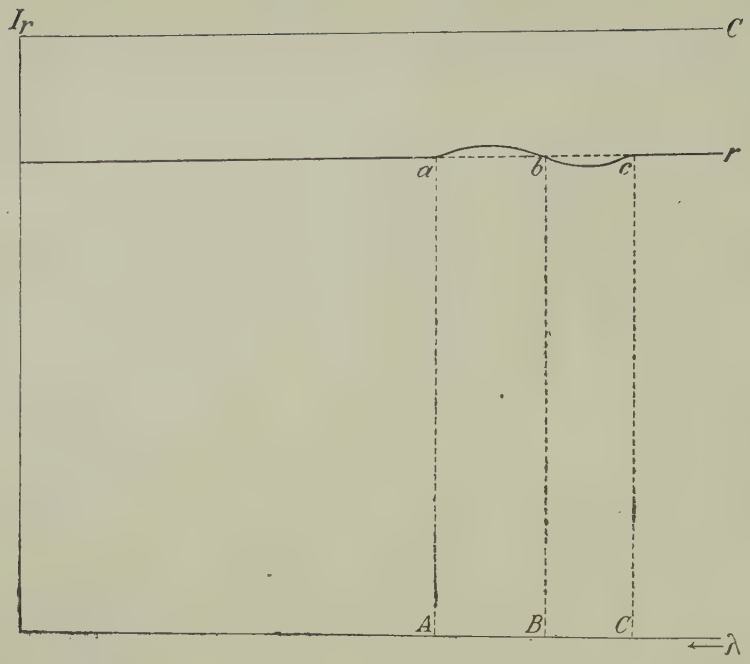


Fig. 4.

radiation for all $= 100$, the relative limb radiation will be represented by the line r in fig. 5. This radiation decreases therefore continu-

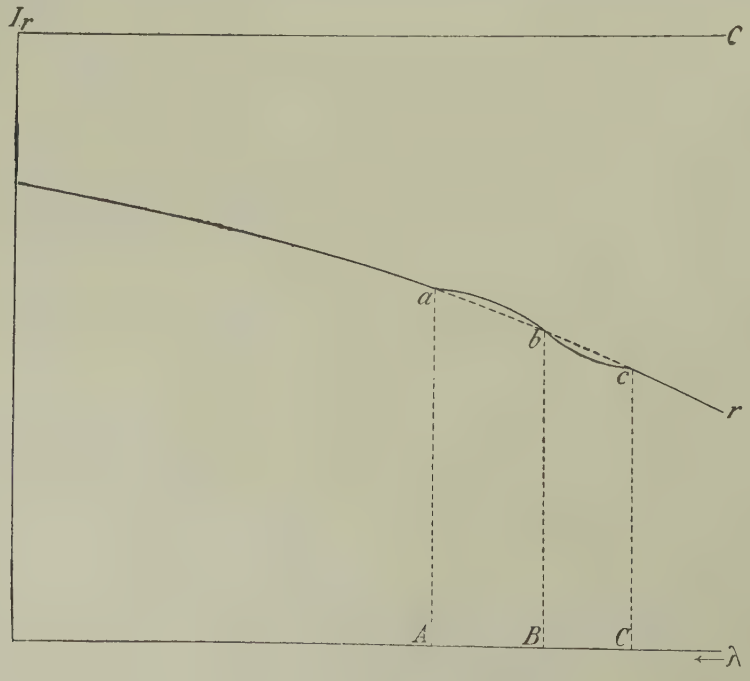


Fig. 5.

ously towards the violet, but presents the same oscillation in the region *ABC*.

Hence the relative distribution of intensity of the light on the sun's disc reckoned with respect to the centre, must present an anomaly in the neighbourhood of the maximum of energy. This anomaly bears entirely the same character and relates to the same region of the spectrum as the anomaly observed by ABBOT (c.f. fig. 5 with fig. 1; the part of the curve r outside C in fig. 5 has not been observed by ABBOT).

Summary. Starting only from the hypothesis that the sun may be conceived as a glowing gaseous body, in which the temperature and the density gradually decrease from the centre outward, and the outer layers of which consist of little luminous, little absorbing, but greatly diffusing and irregularly refracting gas-masses, we have derived an explanation of the anomaly, observed in the decrease of light of different wavelengths from the centre towards the limb of the solar disc.

Chemistry. — *The Phenomenon after Anodic Polarisation.*" I. By Prof. A. SMITS, G. L. C. LA BASTIDE, and J. A. VAN DEN ANDEL. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of March 29, 1919).

Introduction.

When the experimental electrical potential of iron is measured *during* the anodic polarisation, we observe that this potential becomes less negative as the density of the current increases. When this experiment is carried out in solutions containing few or no halogen ions, this phenomenon greatly increases above a definite density of current, and the iron then passes from the active into the passive state. Though this transition from the active into the passive state is not observed for all metals, all of them present, when they are anodes, a potential that is shifted more or less in the positive direction. This phenomenon of the anodic polarisation, like that of the cathodic polarisation, has been explained in a simple way by the recent views about the electromotive equilibria [1]).

A new phenomenon, however, presented itself when somewhat more than two years ago SMITS and LOBRY DE BRUYN made use of a rotating commutator according to LE BLANC [2]) during the anodic polarisation of iron.

This commutator is constructed so that the potential difference is not measured during the passage of the current, but immediately after the current has been broken. With this method of procedure the remarkable phenomenon was discovered that when the current density was not so great that the iron became passive, the iron did not show a less negative, but a *more strongly negative* potential, which means that the iron exhibited a change of the potential *after* anodic polarisation in a direction opposite to that which was to be observed during the passage of the current.

At first it was supposed that this phenomenon had to be attributed to some mistake in the arrangement of the experiment, but it soon appeared that this was not the case, and that the same phenomenon, but slightly modified, also appeared for nickel, and as Dr. ATEN found afterwards, also for chromium [3]).

---

[1]) Zeitschr. f. phys. Chem. **92**, 1 (1916).

[2]) Zeitschr. f. phys. Chem. **5**, 469 (1890).

[3]) These Proc. XX, 1119.

When the experiment was made without the said commutator, and the course of the potential of the iron with the time was examined immediately *after* anodic polarisation, it appeared that after having passed through a minimum, the potential again rapidly rose to the initial value.

As a fuller examination of this phenomenon would have led the investigation of SMITS and LOBRY DE BRUYN into a bye-way, this study was postponed to a later occasion, and this is the reason why the publication of this phenomenon has been withheld until now.

Registration of the Phenomenon.

In order to represent the phenomenon graphically we have employed the photographic registration method, making use of MOLL's galvanometer. The potential of an iron electrode I was measured with respect to another auxiliary iron electrode II, a platinum tin leaf serving as cathode. The electrolyte was a $^1/_2$ normal solution of ferrosulphate. The iron electrode I, which had an area of about 25 m.m^2, was made anode for a short time, the density of the current being chosen so that the iron would have become passive with longer passage of the current. *Immediately* after this anodic polarisation the galvanometer was inserted into the circuit iron I-electrolyte-iron II, so that the course of the potential which iron I presented *after* the anodic polarisation, could be accurately registered.

The film now showed: first the potential of iron I with respect to iron II before the experiment, secondly the curve representing

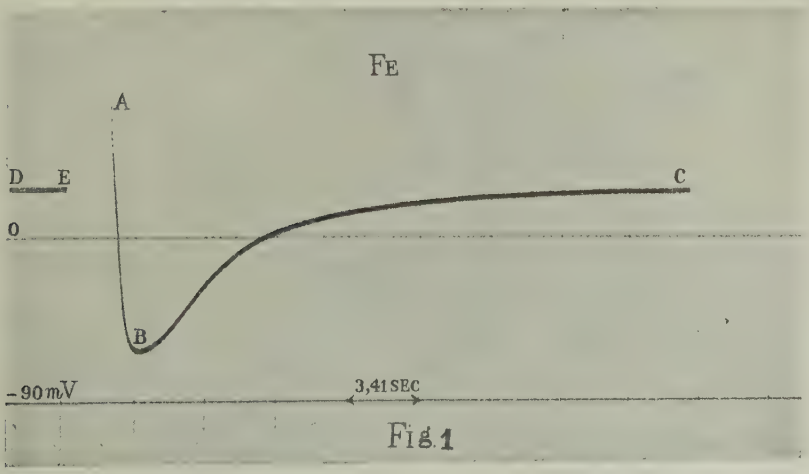


Fig. 1

the course of the phenomenon, thirdly the zero-line, fourthly a line that corresponds to a definite potential difference, and finally time-lines given by a signalling apparatus.

Thus in our experiments with iron in $^1/_2$ N. ferro-sulphate solution the following photographs were obtained.

The line DE represents the potential of iron I with respect to iron II before the anodic polarisation. The other two horizontal lines, which run all over the figure, are the zero-line and the line for -90 milli Volt. The curve A B C represents the phenomenon observed *after* anodic polarisation of iron I with a density of current of $\pm$ 0.360 Amp/cm.^{2}.

The iron electrode I is at first disturbed in noble direction after this anodic polarisation, but this disturbance ceases with great rapidity and the potential descends to a value which is about 90 milli Volt. more negative than the potential before the anodic polarisation. The iron keeps this negative potential only for a short

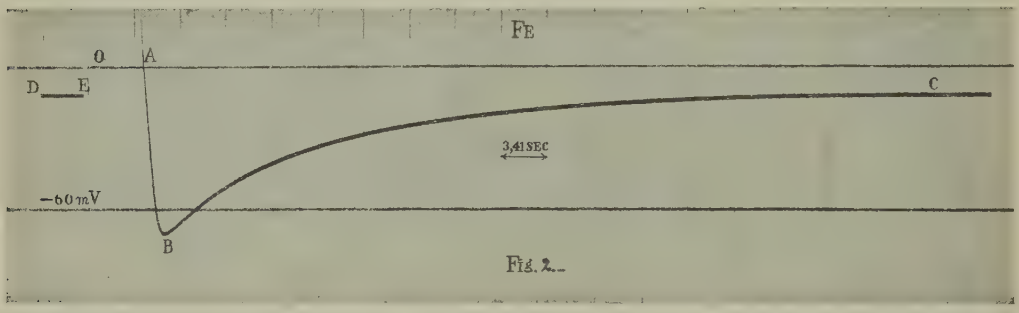


Fig. 2.

time, and rises, first with increasing, then with decreasing rapidity to the value observed before the anodic polarisation.

In fig. 2 the phenomenon has been photographed that was observed when instead of a solution of ferro-sulphate, a solution of $^1/_{10}$ N. ferro-chloride was used. In a few words we may remind here that the increase of concentration in the boundary layer through the short anodic solution has brought about a slight change of the potential in positive direction. In order to find out in how far the found phenomenon is something particular that is caused by the *anodic* polarisation of iron, also the course of the potential of the iron was photographed *after cathodic* polarisation. This photo is reproduced in fig. 3, we see that the iron after cathodic polarisation with a density of current of $\pm$ 0.360 Amp/cm.^{2}. is still pretty greatly disturbed in base direction, the potential of the iron was, namely, in this experiment at first about 80 milli Volt. more negative than before the cathodic polarisation, which potential difference had,

however, almost entirely disappeared again after a minute. We will point out here that a small part of the potential in negative direction

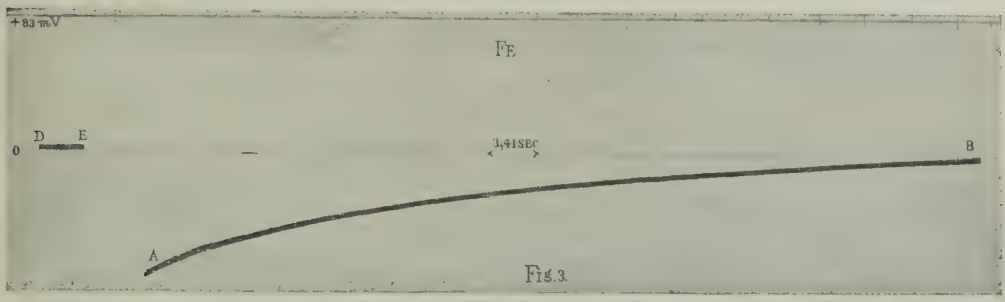


Fig. 3.

is the consequence of the decrease of concentration in the boundary layer during the cathodic deposition of the metal.

As it had appeared before, as has already been mentioned, that nickel, though much more inert, showed the same phenomenon as iron, the same experiments have been made with nickel as with iron, in which the following result was obtained.

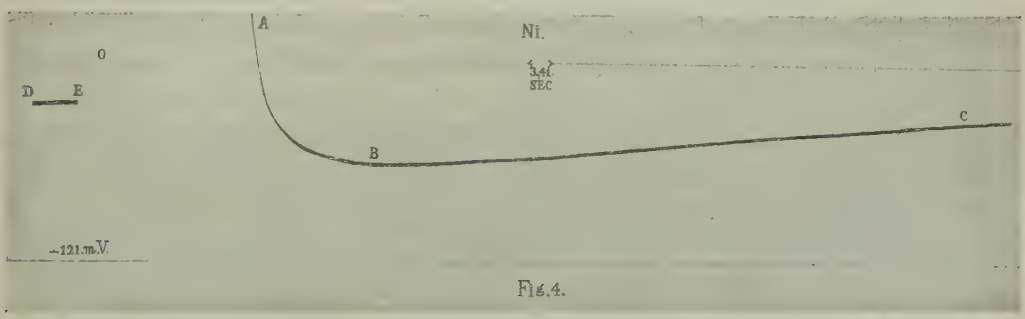


Fig. 4.

Fig. 4 gives the course of the nickel electrode with an area of 80 mm.^{2} in a solution of $^1/_{10}$ N $NiSO_4$ *after anodic* polarisation with a current density of ± 0.075 amp./cm., from which appears that here the same phenomenon is seen as for iron; the potential of the metal becomes more negative after anodic polarisation, and after having reached a minimum value, it slowly returns to the original value of before the anodic polarisation. The phenomenon is the same here as for iron, but it takes place here with much less rapidity.

In fig. 5 the result is recorded of the determination of the potential difference for nickel *after* cathodic polarisation with the same current density.

The nickel is at first pretty greatly disturbed in base direction, the potential is about 240 m.V. more negative than before the cathodic polarisation, but becomes less and less negative with decreasing

rapidity, and does not present the potential of before the cathodic polarisation again until after nearly five minutes. As the whole course occupied so much time, we have made the box with the film execute some revolutions, so that the successive pieces have come above each other on the photo.

It is of importance to state here that RAHTERT [1]), who has also carried out experiments on this subject, found a more negative

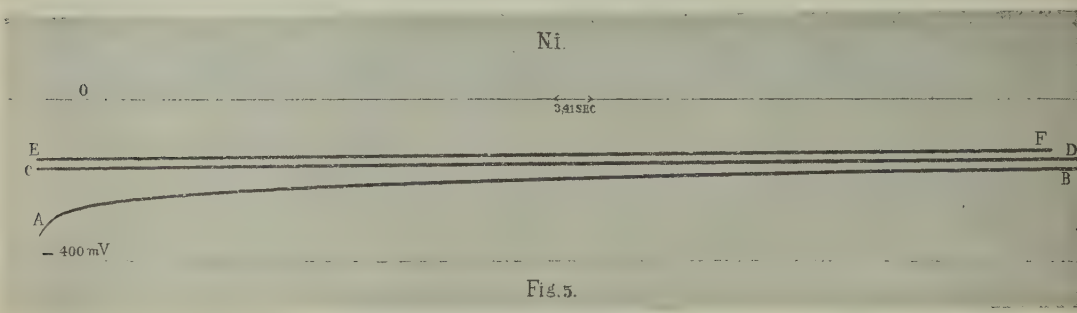


Fig. 5.

potential for nickel *after* anodic polarisation in agreement with us, but after cathodic polarisation a much more positive potential. This is in conflict with what was found by us, and must probably be attributed to a mistake in the arrangement in RAHTERT's investigation. For on earlier occasions the phenomenon photographed in fig. 5 was always found by SMITS and LOBY DE BRUYN and now by us.

As it was of importance to include also a few other metals in our considerations, we have also investigated silver and copper immersed in a silver-nitrate, resp. copper sulphate solution with the following result.

The photo fig. 6 is a reproduction of the potential course of a silver electrode with an area of 42 mm.^{2} in a 0,1 N Ag NO^3-solution after anodic polarisation with a density of current of 0,333 Amp./cm.^{2},

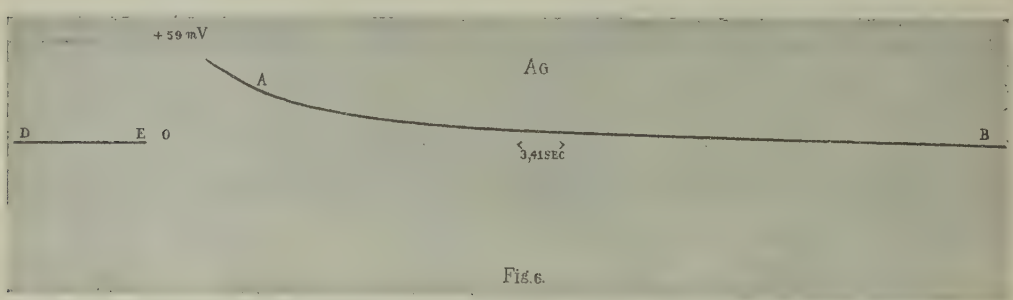


Fig. 6.

[1]) Zeitschr. f. phys. Chem. **86**, 567 (1914).

from which appears that here the ordinary course is found. Also after anodic polarisation the silver has at first a more positive potential, which becomes smaller with continually diminishing velocity.

After cathodic polarisation with the same current density at first a too negative potential is found, which becomes less and less negative, as is shown by the photo fig. 7.

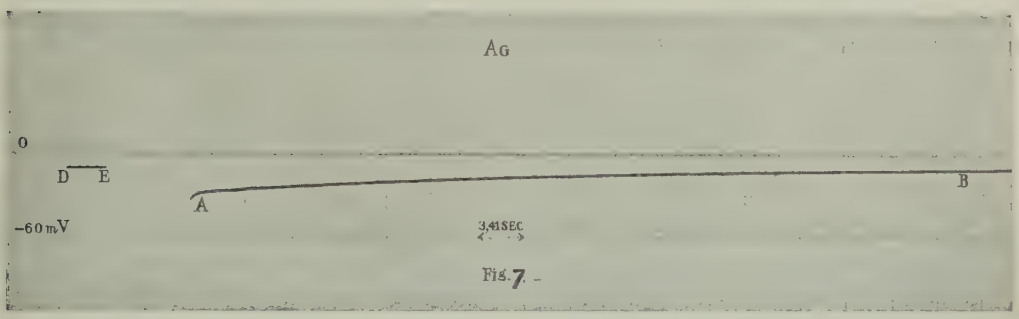


Fig. 7.

Finally also a copper electrode with an area of 9 mm.^{2} in a 0,1 $NCuSO_4$-solution has been examined, and then the same thing was found as for silver in 0.1 N. Ag NO_3, as appears from the photos fig. 8 and fig. 9. The current density amounted here to 0,666 Amp./cm$_2$.

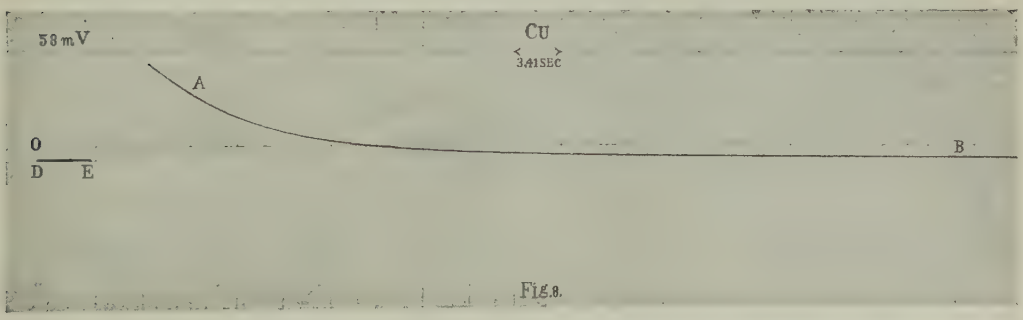


Fig. 8.

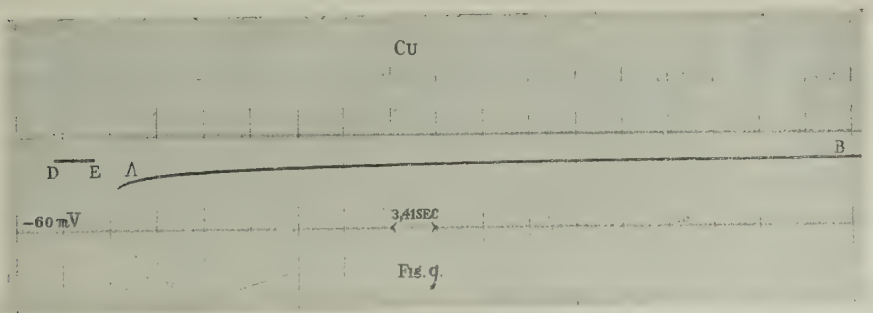


Fig. 9.

So far a deviating behaviour has, therefore, only been found for iron, nickel, and chromium, hence for metals that have ions of different valencies, for this reason it was desirable to examine whether the phenomenon would continue to exist when the ratio of concentration between the different ions in the electrolyte is everywhere so, that the metal can coexist in state of internal equilibrium with this electrolyte. This was investigated for iron by boiling a solution of Ferro-chloride with iron-powder for a long time in the vessel in which the definitive experiment was to be made, leading over pure hydrogen at the same time. The solution thus obtained was 0.6 N.

The result obtained with this solution was convincing in a high

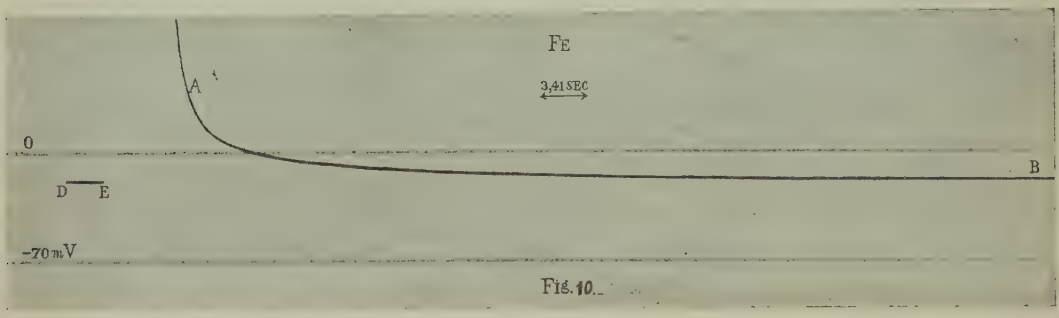


Fig. 10.

degree. As fig. 10 shows after anodic polarisation there was nothing to be seen of a minimum, and at least qualitatively the iron behaved like silver and copper.

It is now natural to assume that also for nickel and chromium the phenomenon can be made to disappear in the same way, about which experiments are now being in progress.

Laboratory for General and Anorg.
Chemistry of the University.

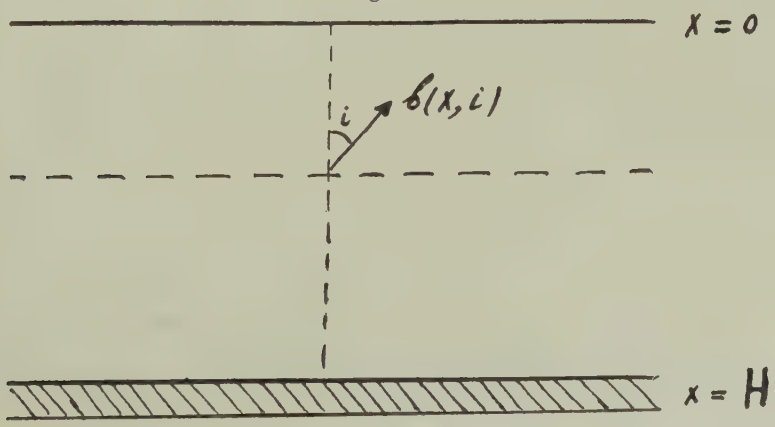
Amsterdam, March 27th 1919.

Physics. — *"On the Effective Temperature of the Sun"*. Some remarks in connection with an article by DEFANT: *"Diffusion und Absorption in der Sonnenatmosphäre."* By H. GROOT. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of March 29, 1919).

In a paper "Ueber Diffusion und Absorption in der Sonnenatmosphäre" (Sitz. Ber. d. Berl. Akad. 1914) SCHWARZSCHILD treated the problem of the radiation of a plain layer, which must be imagined as an absolutely black body, and above which there is an absorbing and dispersive atmosphere. When on a layer (see figure 1) bounded by the planes $x = 0$ and $x = H$ radiation of intensity S, starting from the black body ZZ' falls from all directions, SCHWARZSCHILD denotes by $b(x,i)$ the radiation which passes through the plane x in the same sense as the radiation S, and at an angle i with the normal to the boundary layers, and then tries to find a formula for $b(0,i)$.

Fig. 1.



Black body.

Accordingly $b(0,i)$ is the total intensity of light that passes out at an angle i at the boundary of the atmosphere, and is built up of direct light and light that is dispersed once, twice etc.

SCHWARZSCHILD succeeds in solving this problem for two special cases, and finds:

a. Limiting case of exclusive absorption ($\sigma = 0$):

$$b(0,i) = a + \frac{b \cos i}{k}(1 - e^{-kH \sec i}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

b. Limiting case of exclusive dispersion ($k = 0$):

$$b(0,i) = \frac{0.5 + \cos i}{1 + \sigma H} + \frac{0.5 - \cos i}{1 + \sigma H} e^{-\sigma H \sec i} \quad . \quad . \quad . \quad . \quad (2)$$

Here k = coefficient of absorption, σ = coeff. of diffusion, H = height of the asmosphere, a and b are two numerical constants.

In his article: "Diffusion und Absorption in der Sonnenatmosphäre" (Sitz. Ber. d. K. Akad. zu Wien, Abh. II*a*. Bnd. 125 (1914)). A. Defant by the aid of data which he derives from Abbot's observations on the decrease of the intensity of radiation on the sun's disc from the centre towards the limb (Annals of the Astr. Observ. of Smithsonian Inst. Vol. III, Washington 1913, p. 158), tries to decide which of the two causes, absorption or dispersion, appears to be most active on the sun.

By means of a kind of "trial and error" method he succeeds in deriving a formula:

$$b(0,i) = \frac{0.5 + \cos i + e^{-0.0405\,\lambda^{-4}\sec i}(0.5 - \cos i) - 0.3804 + 0.3136\cos i}{1 + 0.0405\,\lambda^{-4}} \quad . \quad (3)$$

which is halfway between (1) and (2) and yields numerically accurate values. This seems to point to this that the diffusion effect by far preponderates, but is yet influenced by a slight absorption.

In how far the considerations through which he arrives at formula (3), are of value, must be left undecided here. It is certain that the numerical values are pretty accurate, as table I shows convincingly.

TABLE I.

$\cos i$	$\lambda = 0.433\ \mu$			$\lambda = 0.604\ \mu$			$\lambda = 1.031\ \mu$		
	$b(0,i)$	$b(0,i) \times 355$	Observed value	$b(0.i)$	$b(0,i) \times 375$	Observed value	$b(0.i)$	$b(0.i) \times 117$	Observed value
1.0	1.2752	453	456	1.0643	399	399	0.9486	111	111
0.9	1.1906	423	419	1.0164	381	380	0.9175	107	107
0.8	1.0996	390	384	0.9656	361	360	0.8838	103	105
0.7	1.0006	355	348	0.9097	341	337	0.8491	99.4	100
0.6	0.8932	317	309	0.8476	318	313	0.8137	95.2	95.8
0.5	0.7764	276	277	0.7764	291	288	0.7765	90.9	90.0
0.4	0.6506	231	238	0.6917	259	265	0.7366	86.2	86.2
0.3	0.5180	184	192	0.5863	220	230	0.6912	80.9	80.9

Explanation of table I:
In this table $b(0,i)$ calculated for the values of $\cos i$ is given in the first column for three different values of λ by the aid of (3). In column 3 the found values of $b(0,i)$ have been multiplied by a factor in order to render a comparison with ABBOT's values, recorded in the fourth column, possible.

By the aid of (3) and ABBOT's values, which I subjoin, DEFANT tries to draw a conclusion on the effective temperature of the sun.

Wavelength in μ	Radiation in the centre of the sun's disc.
0.323	144
0.386	338
0.433	456
0.456	515
0.481	511
0.501	489
0.534	463
0.604	399
0.670	333
0.699	307
0.866	174
1.031	111
1.225	77.6
1.655	39.5
2.097	14.0

(ABBOT's values).

His reasoning is as follows:

For $i = 0$ we obtain $b(0,0)$ i.e. formula (3) then gives for every wavelength λ the intensity of radiation passing out in the centre of the sun's disc, when that of the area of the photosphere for this λ is put equal to 1. What we measure is, however, not the quantity $b(0,0)$, but the radiation i_λ, actually passing out, which is in relation with $b(0,0)$ through the formula:

$$I_\lambda = \frac{i_\lambda}{b(0,0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which I_λ is the intensity of radiation in the spectrum of the photosphere (considered as absolutely black body) for the wavelength λ.

By the aid of (3) and (4) and ABBOT's values the following table can, therefore, be calculated for I_λ (table II). According to our

supposition the photosphere radiates as an absolutely black body, so that PLANCK's formula may be applied, according to which [1]):

$$I_\lambda = \frac{7.211 \times 10^8}{\lambda^5 \left(10^{\frac{2.1563 \times 2890}{\lambda T}} - 1\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The quantities I_λ from the table are expressed in an unknown unity. When we consider this unity and T as unknown quantities, then T can be solved from two values of I_λ (for λ_1 and λ_2 e.g.).

If our basis is correct, we must find the same temperature from all combinations in pairs of I_λ.

DEFANT calculates T from the combinations

$$\left.\begin{array}{ll} \lambda_1 = 0.5 & I_\lambda = 700 \\ \lambda_2 = 0.9 & I_\lambda = 180 \end{array}\right\} T = 8900°$$

and

$$\left.\begin{array}{ll} \lambda_1 = 0.6 & I_\lambda = 350 \\ \lambda_2 = 1.2 & I_\lambda = 90 \end{array}\right\} T = 8700°$$

and considers the agreement "genügend". (loc. cit. p. 517).

TABLE II.

Wavelength λ	$1 + 0.0405\ \lambda^{-4}$	$b(0,0)$	i_λ	I_λ
0.323	4.721	0.299	144	481.8
0.386	2.824	0.479	338	705.7
0.433	2.152	0.593	456	769.5
0.456	1.937	0.644	515	799.8
0.481	1.757	0.682	511	748.9
0.501	1.646	0.710	489	688.7
0.534	1.498	0.737	463	628.1
0.604	1.304	0.816	399	500.2
0.670	1.201	0.853	333	390.5
0.699	1.170	0.864	307	355.2
0.866	1.072	0.903	174	192.8
1.031	1.036	0.918	111	120.9
1.225	1.018	0.926	77.6	83.8
1.655	1.005_4	0.931	39.5	42.4
2.097	1.002_1	0.932	14.0	15.0

[1]) The constants are those used by DEFANT.

Unfortunately, however, a fatal error has slipped in. For to $\lambda = 0.6$ does not correspond $I_\lambda = 350$, but — (interpolating graphically) — $I_\lambda = 506$, which yields $T = 6600°$ instead of 8700°, so that agreement is out of the question.

A serious objection to the whole method seems perfectly obvious to me, namely this:

The assumption that all kinds of light come to us from one photospheric surface, in other words that light of various wavelengths should come from the same depth of the sun, appears more and more untenable in the light of recent researches (see e.g. the thesis for the doctorate of J. SPIJKERBOER "Verstrooiing van licht en intensiteitsverdeeling over de zonneschijf" (1917) (Dispersion of light and Distribution of Intensity over the Sun's Disc)). If, however, in reality light of different wavelengths originates from different parts of the sun, it becomes very questionable whether we shall be allowed to apply PLANCK's formula, as we saw DEFANT do. For this would mean that we supposed every kind of light to have, as it were, a kind of "photosphere of its own", which radiates as a black body, the photosphere for the greater wavelengths lying deeper than that for the smaller. It might then be expected that the temperature determined with PLANCK's formula, becomes a function of λ, i. e. *T would be the greater as λ increases.*

In this latter remark we have a means to investigate whether the hypothesis that the photospheres overlap each other like scales can find a semblance of justification.

By graphical interpolation from the values of table II I construed table III:

TABLE III.

λ	I_λ	λ	I_λ	λ	I_λ	λ	I_λ
0.40	709	0.70	342	1.00	134	1.60	46
0.45	791	0.75	284	1.10	104	1.70	39
0.50	714	0.80	239	1.20	87	1.80	32
0.55	604	0.85	201	1.30	74	1.90	25
0.60	506	0.90	174	1.40	64	2.00	19
0.65	418	0.95	153	1.50	55		

As we do not know the unity in which I_λ is expressed, we require, as was already remarked before, always two values of I_λ (a_1 and a_2) to find T.

The calculation comes to this:

Let A be $= 7.210 \times 10^8$, $\beta = 2.1563 \times 2890$, a_1 and a_2 the values of I_λ corresponding to λ_1 and λ_2, f an unknown factor dependent on the unities in which I_λ has been measured. Then the following equations hold:

$$a_1 f = \frac{A}{\lambda_1^5\left(10^{\frac{\beta}{\lambda_1 T}}-1\right)} \quad \text{and} \quad a_2 f = \frac{A}{\lambda_2^5\left(10^{\frac{\beta}{\lambda_2 T}}-1\right)} \quad . \quad . \quad . \quad (6)$$

When we choose the values of λ so that $\lambda_2 = 2\lambda_1$, and when we put $10^{\frac{\beta}{\lambda_2 T}} = x$, we easily get:

$$\left(\frac{a_2}{a_1}\right)\left(\frac{\lambda_1}{\lambda_2}\right)^5 (x^2-1) = x+1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The root $x = 1$ yields $T = \infty$, has therefore no physical meaning, so that we find T from:

$$\left.\begin{aligned} x &= 32\left(\frac{a_2}{a_1}\right) - 1 \\ T &= \frac{\beta}{\lambda_2 \, lg \, x} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In this way I found:

$\lambda_2 =$	0.8	0.9	1.0	1.1	1.2	1 3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$T =$	7200	8800	8900	8500	7900	7200	6300	5800	5500	5100	5000	5200	5700

hence on an average *a decrease of T with increase of* λ (see diagram I).

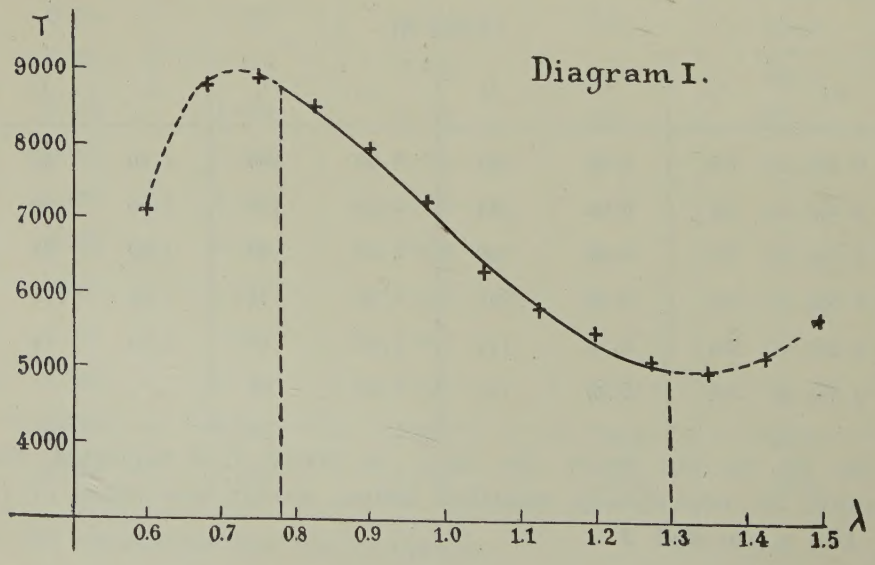


Diagram I.

Nor is this manner entirely satisfactory; for now we do not know to what λ the found T should properly speaking belong, because the two values of λ (λ_1 and λ_2), which are required, can lie pretty far apart in this way of calculation. Does for ($\lambda_1 = 0.9$, $\lambda_2 = 1.8$) T e. g. belong to λ_1, to λ_2, or to a value lying somewhere between λ_1 and λ_2?

When we want to avoid this difficulty, we may treat the equations (6) as follows:

Let $\lambda_1 : \lambda_2$ be $= n : m$ or

$$\left.\begin{aligned}\lambda_1 &= \frac{\varrho}{m}\\ \lambda_2 &= \frac{\varrho}{n}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (9)$$

we find easily:

$$10^{\frac{m\beta}{\rho T}} - 1 = \left(\frac{\alpha_2}{\alpha_1}\right)\left(\frac{m}{n}\right)^5\left(10^{\frac{n\beta}{\rho T}} - 1\right) \quad \ldots\ldots \quad (10)$$

Put:

$$10^{\frac{\beta}{\rho T}} = z \qquad \left(\frac{\alpha_2}{\alpha_1}\right)\left(\frac{m}{n}\right)^5 = C \quad \ldots\ldots \quad (11)$$

then (10) passes into:

$$z^m - Cz^n + (C-1) = 0 \quad \ldots\ldots\ldots \quad (12)$$

When we take care that m is $= n+1$, the shape becomes somewhat more suitable for numerical approximation, namely:

$$z^n(z-C) + (C-1) = 0 \quad \ldots\ldots\ldots \quad (12a)$$

When z has been sufficiently closely approximated, T follows from:

$$T = \frac{\beta}{\varrho \, lg \, z} \quad \ldots\ldots\ldots\ldots \quad (13)$$

In this way λ_1 and λ_2 can be brought close enough together to exclude indefiniteness in the choice of the λ to which T belongs.

Thus we found:

λ_1	0.4	0.5	0.6	0.7	0.8	1.0	1.2	1.5	1.8
λ_2	0.5	0.6	0.7	0.8	1.0	1.2	1.5	1.8	2.0
T	(6400)	9000	10.000	9600	8000	5500	3800	5400	–

so that on an average:

$\lambda = 0.5-0.7$	$T = 9500$
$0.7-1.2$	6000
$1.2-1.8$	4600

hence a similar result as for the first method. (See diagram II). The deviations inter se are now much larger, as was, indeed, to be

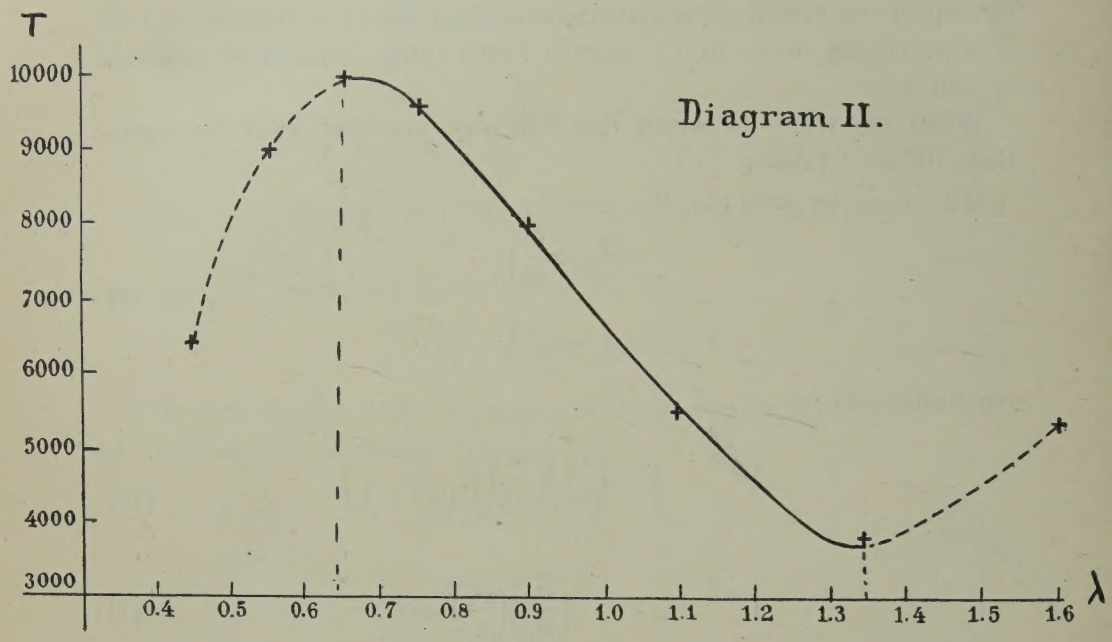


Diagram II.

expected, as on the small intervals λ_1—λ_2 the inevitable errors in I_λ (an experimental quantity!) make themselves very greatly felt.

Thus $\left.\begin{matrix}\lambda_1 = 1\,8\\ \lambda_2 = 2.0\end{matrix}\right\}$ give an imaginary value for T, but when for $\lambda_2 = 2{,}0$ $I_\lambda = 22$ is taken instead of $I_\lambda = 19$, then T would become $= 18000°$.

In this manner particularly the smaller values of I_λ are unfavourable, hence the values for $\lambda_1 = 1{,}5$ and $\lambda_1 = 1.8$ are not much to be trusted.

The values of I_λ for $\lambda < 0{,}5$ are strictly speaking also unreliable, because the graphical interpolation — as indeed every other too — becomes very inaccurate here.

When we leave all these doubtful values of T out of consideration we come to the result that particularly in the region of the reliable values of T (the full line in the diagram) *there is an unmistakable tendency of T to decrease on the increase of λ, hence exactly the reverse of what we thought we might expect a priori.*

In a following paper I propose to discuss the question to what this unexpected result is to be attributed.

Utrecht, March 1919.